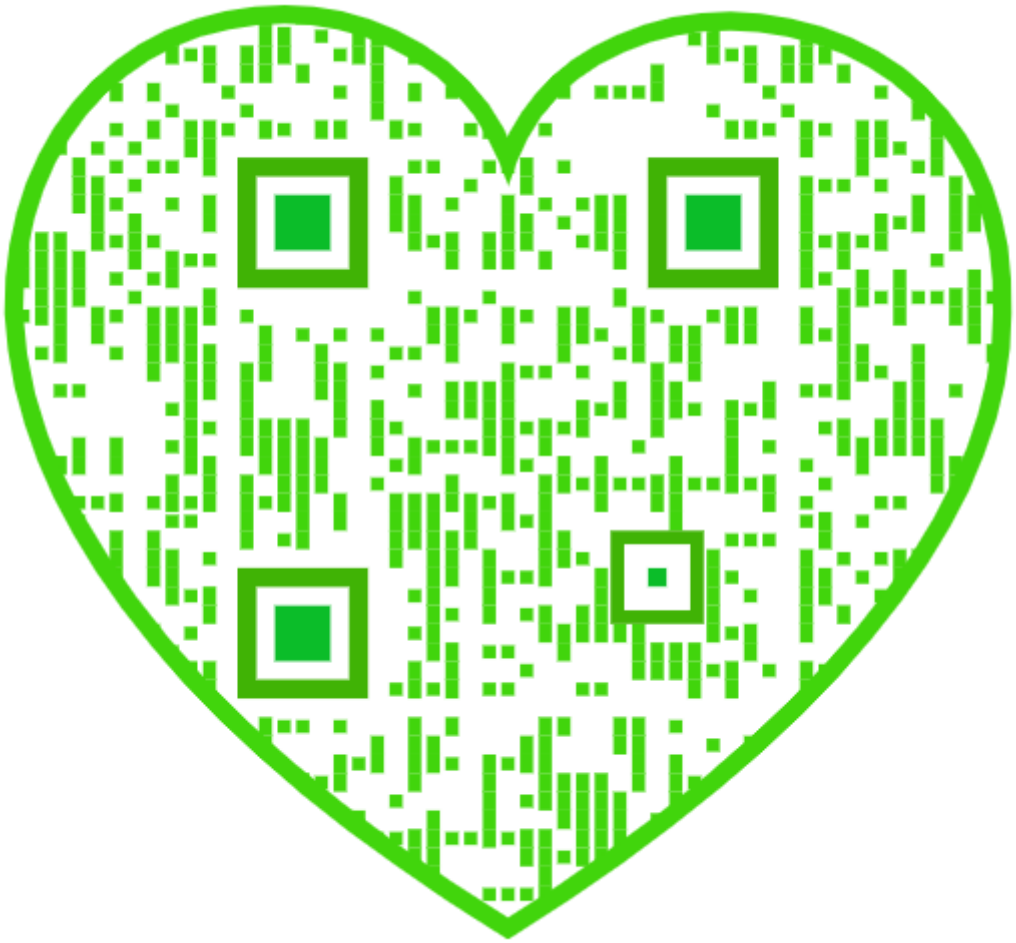

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The American Leather Chemists Association

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DETERMINATION OF COLOR VALUES.[1]

By George A. Kerr.

As the Chairman of this Committee understands it, the end to be attained and most desired by the investigation of the color values of tanning materials, is the evolution of a method whereby the color quality and color volume or density can be positively determined and the results expressed in terms of measurement, or numbers which admit of comparison.

Upon taking up the subject on these lines, the difficulty of finding a starting point which might reasonably be expected to lead to some definite results was at once experienced. The preva-

[1] Preliminary Report of 1908 Committee.

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lent skiver method is undoubtedly unsatisfactory, if comparative results and the qualitative and quantitative determination of color are desired. It is true, the skiver has its value in the hands of the individual in many ways about the tanner's laboratory, but as a comparative test it is of little value.

Assuming that everyone interested in this subject has experienced the difficulties of striking a uniform color on a hide, either in tanning or in dyeing it after it is tanned, it is obvious that the same difficulties will be met in tanning small pieces of sheep or calf skin. The variation in texture and thickness of the skin are sufficiently great to preclude all prospect of two or more laboratories obtaining comparative results on a given sample of tanning material. Even were it possible for everyone to identically prepare the skin for tanning, and then tan it under absolute conditions, this objection is sufficient to condemn its use as a standard method of determining color. However, if further objections are necessary, they are not wanting, and feeling assured of the futility of going further with skiver tests, nothing was done in this direction.

The use of hide powder has been suggested, and also the use of mordanted or unmordanted textiles. Like the skiver, they are useful in various ways, but leave final results to the imagination, for, granting the methods of their employment are susceptible of refinement until any number of operators can produce comparative tests, they fail to convey the knowledge of how much better or worse one sample tested is than another, or indicate the variation in the component color elements, which causes the difference in the color produced.

Some work has been done this year in the direction of making dye tests upon cotton cloth by Mr. H. C. Reed, and the writer, which indicates that it is possible to obtain much more uniform and concordant dye-tests in this way than by the skiver method. Sufficient work has not been done at this time, however, to recommend the adoption of cotton cloth for the skiver, but if we are compelled to be satisfied with dye tests as a means of estimating color values, it apparently possesses the advantages of being readily obtainable, of uniform texture and quality, and

obviates the necessity of special preparation previous to use. It also yields greater distinction in tones than the skiver.

Next to the skiver method, the use of the Lovibond tintometer appears to be the most common method employed for measuring color, and at first glance, it appeals to the leather chemist as a probable solution of this problem. Finding no record of any comparative work in this direction, it was decided to make the attempt, and accordingly samples and instructions were sent to the members of the committee having tintometers at their disposal.

The samples of tanning material were analyzed previous to being sent out, and the analysis marked on the label, so that uniform solutions would be employed by everyone participating in the work. The other directions were simple and offered no opportunity for misunderstanding; therefore, there was every reason to believe the results would throw some light upon the value of this instrument.

Three members of the committee sent in reports, and I regret to say they were nothing short of bewildering in their variations, a comparative interpretation being well-nigh impossible. Considering the standard of ability represented by the personnel of the committee sending in reports, I am rather dubious regarding the value of the tintometer as the basis of a universal method.

Three series of tests were asked for. The first consisted of determining the color components of two solutions of the same tanning materials of different tannin contents, determinations being made under the ordinary laboratory conditions as to illumination. For the second series, the same solutions were used, artificial light instead of daylight being employed, and the instrument screened to avoid the influence of external light, reflected or direct. Notwithstanding the lack of concordance and comparative value of these results, they make clear several conditions which must be observed in the use of the Lovibond tintometer, before either concordance or uniformity can be expected. It is important that the illumination of the cell containing the material examined and the glass slides employed to match the color be under control. The light should be invariably neutral

(white), of a constant intensity, and the reflector free from external influences such as reflection from colored walls, buildings, or objects in the room where the test is conducted. In short, the work should be conducted in a dark room, with dead black walls and ceiling, and no other light than that used for the illumination of the apparatus should be admitted, while the test is being made.

Quite as important is the standardization of the solution to be examined. The color determination of a tanning material can only be of value when its relation to the tanning contents is established; therefore it is necessary to ascertain, with the utmost accuracy possible, such contents. Just how much of an obstacle this feature will prove, cannot well be estimated until it becomes possible for a number of operators to obtain comparative results on identical solutions.

Noting the great variations in the results of the tests made, it occurred to the writer, that some of the trouble might be ascribed to the difference in individual sensitiveness to color tones, or to color-blindness in a certain degree, but upon looking into the matter he finds that less than five per cent. of male adults examined are unable to distinguish even very fine distinctions in shades of color. If this is true, it would seem that by standardizing all the conditions governing tintometer tests, including the instruments used, there should be some possibility of making them both concordant and comparative.

Assuming that the tintometer could be made to yield satisfactory results, it only furnishes a partial solution of the color question, and although we may ascertain the numbers representing the color components of a solution of tanning material, we still fail to get any measurement of the color density, the difference in color components not being indicative of the depth of shade produced upon leather.

With the idea of ascertaining whether or not color density could be measured, the writer considered the use of the photometer for this purpose, and after quite a series of experiments, finds that with a specially designed photometer, the volume of light transmitted by a tannin solution can be accurately measured against a standard, and expressed in terms which admit of in-

telligent interpretation. It would be premature to describe this instrument now, as much remains to be done in the way of perfecting its application to this work, but it is hoped that it may eventually be developed so that both color quality and color density can be determined with the same instrument at the same time.

In conclusion, I would recommend that inasmuch as it has taken all the time available this year to get the consideration of this question fairly started, that the present committee be allowed to stand another year.

DISCUSSION

MR. WILSON: I think Kerr's method of measuring color, and also the tintometer method, are very instructive both to the chemist and the extract man, but it is hard to induce the tanner that it is any good to him. He wants something he can feel. The sheepskin is always their guide. We all know it is not the real, true color of the extract. I tried the other method for awhile, and they didn't want that. They wanted to feel it, and maybe taste it.

MR. KERR: I grant the skiver has its value. I use them and will probably continue to use them. The point I want to make is this: If the tanner does prefer one grade of extract over another we will never convince him of it or any one else. He sees whether he is getting a good article or a poor article, but the man who is producing it does not stand a show. It is absolutely meaningless to him. Now if a tanner buys a consignment of extract and you have a tintometer and make a measurement of it and it is specified there by figures and numbers, don't you see, and every shipment that comes in is examined by his chemist and the numbers compared,—he knows he is getting a standard grade all the time. The colors of skivers may vary, but if his instruments are accurate or as nearly so as may be, then it protects both him and the man who is supplying him the goods, because you know, or at least I know in my own experience, every once in a while a tanner will send us two pieces of skiver and say, "Here is what you have been shipping us. Here is a skiver from the chemist. Your color is off." As a matter of fact the color is not off. I tell him it is not off; that my eyesight is better than his skiver. I live with my extract day in and day out and if it changes I know it. The result is I pay absolutely no attention to variations in skivers. I wouldn't allow a man 15 cents on a tank car of extract if the skivers differed, unless the differences in color were caused by contamination. That is a different matter.

MR. ALSOP: I use a grain split of cow hide, which I think is better than a skiver. It gives more uniform tests.

MR. KERR: You get probably a more uniform texture.

MR. ALSOP: I use a grain split.

MR. KERR: From a cow hide? How heavy is it?

MR. ALSOP: Just a little heavier than a skiver.

MR. KERR: I had occasion to examine a good many tests of that kind made on calfskin some time ago and of course the colors ranged from good to bad.

MR. ALSOP: Calfskins act very differently from the cow hide split. I have tried them out very thoroughly. They vary worse than sheepskins.

MR. KERR: In this case what attracted my attention was not the variation in the texture of the hide but in the preparation of the skin. Some of them had been thoroughly de-limed and cleaned, and other skivers I examined you could take your knife and cut them and they showed chocolate colored, which is indicative, of course, of the beam work on the skin.

MR. SMALL: I have been using the same thing Alsop speaks of, namely, grain split from the cow hide, ever since I started making skiver tests, and I find them very distinctly satisfactory. It is much the best of anything I have been able to get hold of in the way of color value determination.

MR. KERR: How is the grain prepared after you get the grain split?

MR. SMALL: I get it split in the lime stage and work it out thoroughly—work it in the borophenol solution. Of course immediately before using it it is washed in running water until there is no odor of phenol left in it, and then it is used.

MR. WILSON: How long does it take to tan them, Mr. Small?

MR. SMALL: I usually take three days to finish mine up. Of course you can set your color in a smaller time. If you want to put it in a churn and rotate it you can make your color test as quickly as you can in a skiver. I think there is a little information gained relative to the tanning values of the extract by giving a little more time in the liquor and letting it tan out so that you really get a piece of leather out of it. My splits are apt to run rather heavier than I should judge Alsop's do, from what he says.

MR. NORRIS: In preserving your grain splits do you put in a salt solution?

MR. SMALL: No; they go into this borophenol solution. That is the only chemical they meet all the way through. The skin, as I say is taken from the lime and split. Then this grain split that I get is put into a borophenol solution and that serves as a bait—removes the lime. The split then is taken and soaked and scudded and then cut up and the pieces of the size for my color tests are then put into a fresh borophenol solution and they stay in there, and they will keep as long as you want them to. I have kept them for a year or two and as far as I could see they appeared no different at the end of the year. The only treatment they need after that is simply to take them and wash the

borophenol solution out by soaking them in water, changing your water frequently, squeezing them and putting them back in again, until the borophenol is all washed out; and the best test I have found for that is your nose. The phenol of course has a very strong odor.

MR. NORRIS: In the tanning process do you use a shake method or lay away in trays?

MR. SMALL: I start out with one containing about ¼ per cent tannin and let the colors strike from that fairly well. Then strengthen up to ½, then 1 per cent; then top off with 5 per cent, figuring on the actual tanning content of the material I am testing—on the barkometer test. I usually take a matter of three days for the tanning process. That is, the method I actually follow is to take the skin and wash it and soak it over night in water. then slick it out and oil half of it and leave the other half un-oiled. I then take it out and dry it, the idea being to get the two shades. You do get a difference in shade from your oiled skin and the skin that is not oiled, and I prefer to do that in order to get both color values.

MR. CARR: Do you dry them in the dark?

MR. SMALL: Yes; well, not an absolutely dark room, but I put it in a closet; no direct sunlight comes in,—nothing but diffused light through the cracks.

MR. NORRIS: Do you find much difference between that method you follow and the shake method; that is, tanning in a short time? Do you find any marked differences in shade?

MR. SMALL: I have made no comparative tests. I see no reason why the shake method would not work perfectly well; the only reason I do not use it is that I have not a shaking apparatus that adapts itself comfortably to that style of work.

MR. NORRIS: The only objection I see is the length of time.

MR. SMALL: That of course is true of commercial work. For my purpose I can tell at the end of an hour or two after the skin has been in the tanning solution whether it is sufficiently bad so that it needs to be condemned, and if that is not the case, why it is nothing more than merely—there is no hurry about it from my point of view. But I see no reason why if one is in a hurry the thing cannot be hurried up by carrying your process through in a shaker. Of course it is going to take a longer time with a thicker piece of pelt than it is with a thin piece. You cannot get away from that, and it will require more care both in soaking and the drying and all the rest; so that for rapidity the method has not very much in its favor. But for accuracy, for comparative results, I would vastly prefer it to anything I have been able to work out or anything I have seen in the way of color tests on skivers of any sort in any other laboratory.

MR. CARR: Is it necessary to be very careful to get out that last 5 per cent liquor?

MR. SMALL: Yes; but by soaking over night it leaves it very uniform.

MR. SMALL: What is your experience, Mr. Alsop, with regard to the grain split. Can't you detect differences comparatively small in different shipments from the same source and separate shipments from different sources. It seems to me that I can.

MR. ALSOP: Yes, and I think that with a grain split from a cow hide you can work pretty nearly as quick as you can with a skiver.

MR. SMALL: Any suggestions that any of you have to offer with regard to the work of the Committee on the Determination of the Color Value of Tanning Materials would be very much in order now, and I should be pleased to hear from any of you who have any suggestions to offer.

MR. CARR: Probably there is a great deal to favor in the argument that the color should be shown on the pelt if possible, and I would suggest that both Mr. Small and Mr. Alsop write out accurate detailed descriptions of their methods and have the Committee handle them, and that in their work, instead of trying to determine the color of any particular extract, they make various—even grotesque—mixtures in order to determine whether there is a fine line between the different values. That is to say, make various proportionate mixtures of hemlock, quebracho, chestnut, oak—and let the series of colors of the skivers show whether any difference can be shown in that respect. There would be then mixed a large variety of color qualities as well as color densities. It seemed to me too that in regard to your particular method it might be well to trace out whether tanning directly from the borophenol solution will have any bearing on the result. If any bearing, what relation that bearing has to any degree or percentage of borophenol still remaining, and by rather a laborious line of comparison determine whether there is any possibility of pelt showing fine lines of distinction both in color density and quality of color. Practically all of us have been accustomed to putting the color upon pelt in some form, either on the grain split from the cow hide or sheepskin, and lately the idea of staining textiles. It seems to me the first effort should be made, so far as the effort to reconcile the desires of the extract manufacturer and the tanner is concerned, toward the pelt. I would not consider it at all desirable to abandon photometric methods, because they appear to have the potentiality of a great development, but the pelt it seems to me should be for the time being the thing to strike at

MR. SMALL: Speaking personally, I would say that I think it is never going to be satisfactory to the tanner to have any method of color determination which is mathematically expressed. I think he is always going to want some visual interpretation for his guidance. Therefore I do not believe that any photometric method or tintometer method by itself will be satisfactory. I do think that a method of color comparison on the lines of the photometer or tintometer or a combination of the two, has its place, and that our Committee should work along

both those lines, first with the idea of securing the best method of setting the color on some material—pelt or wool or whatever it may be—whatever substance can be found that will take the color and give a visual presentation of it to the user; and secondly, some sort of instrument for arriving at a mathematical expression of the color value.

FORESTRY.[1]

By H. S. Graves.

At the time of the first settlement of the United States there was a forest unexcelled anywhere in the world. It stretched in an unbroken mass from the Atlantic Ocean to the prairies. It covered a large portion of the Rocky Mountains, and there was a broad band of forest on the Pacific Coast. Our original forests were remarkable not only for their vast extent but also for the great number of valuable species constituting them. The richness of our forest flora is due in part to the fact that the country includes several climatic zones and in part also to the fact that the climate and physiography have favored the development and continuance of tree life. And so it happened that many genera of trees are found in America which were exterminated in Europe in glacial periods. For example, cypress, magnolia, catalpa, red gum, hemlock, cedar, walnut, and redwood. Another characteristic of our original forest was the enormous yield in valuable material. The greater part of the country is comprised within the temperate zone which, coupled with excellent moisture conditions, favors rapid growth and large development of trees. The original forest contained trees of great age and enormous size. Nature working through centuries had provided a vast storehouse of timber, full grown and ready for use when required. It is on this supply that the American people have been drawing for four centuries, and it has constituted a source of great wealth and has been an important element in the internal development of the country. When the country was first settled the effort was to clear the land for agriculture. With the increase of population there naturally arose a demand for forest products and the timber was cut for use rather than merely destroyed. The first lum-

[1] Address delivered at 1908 Boston Convention.

bering for use naturally took only the choicest trees in the forest. Timber was so plentiful that the ordinary grades had no value. The selection of a tree here and there had little effect on the forest. In fact, the cutting was beneficial, for it removed and utilized the mature trees, and the openings which were made induced new growth, thereby increasing the increment of the forest. As the demand for timber increased for export and for local consumption and as the supply of the best grades of timber became more remote, the forest near the settlements was cut over a second time, and this process went on until the modern systems of lumbering were introduced, which made very heavy inroads into the forest and in some cases removed every tree. It was soon after the lumbering for use began that the forest fires became a common occurrence and these increased in number and severity, burning over the majority of lumbered lands and usually enormous areas which had not been cut, and destroying millions of dollars worth of timber. It has been only within the last few years that such fires have to any degree been checked. It is a fact that with forest destruction by lumbering and fire there follows also enormous destruction by insects.

Hitherto the only idea in the minds of the American people has been to utilize the great store of timber which they had received as a heritage. The Government and States disposed of their lands as rapidly as possible to private owners and for private exploitation. Private owners in handling their forest lands had no other idea than to cut the accumulated stock without any regard whatever for future growth. While a few far-sighted lumbermen in Maine and a few other sections began 30 to 40 years ago to restrict their cuttings to only the oldest timber and reserve the intermediate and young growth, and while a few individuals planted trees and practiced forestry in a small way, it is only within a decade that there has been any considerable conception of the management of timberlands on a large scale with a view of perpetuating the forest growth.

There never was a nation so lavish in its use of wood and timber. This is due in part to the wonderful growth of the country and the requirements for lumber for new buildings,

cars and other construction work. The great development of the transportation systems of the country have brought to market comparatively cheap material, and the people have acquired the habit of extravagance in its use. Figures of annual consumption are so great as to be meaningless to most persons. We are using now for lumber alone 40,000,000,000 feet board measure per year. That figure is so great that to anyone who is not handling lumber on a large scale it means comparatively little. Some of you may be familiar with the best forests of spruce in the White Mountains, or with the long leaf pine of the South. Imagine the best of this cut clear in one place; there would be required 4,000,000 acres to meet the annual requirements of this country. But that would be lumber alone, and would not include shingles, which would require 200,000 acres more. It does not include the railroad ties, of which we use 100,000,000 a year. There would have to be added also the timber used in cooperage, for mine props, for lath, for veneer, for paper, and for poles and for chemical by-products. We use 3,000,000 poles a year, and for paper pulp not less than 3,000,000 cords; and these figures do not include the wood used for fuel, which has been variously estimated from 50 to 100 million cords a year.

There has been a wonderful development of the lumber industry in recent years. American ingenuity has devised mechanical methods of extracting logs from the forest with great rapidity. The value of manufactured lumber has risen much more rapidly than the value of the forests. In consequence there has been a tremendous rush to purchase land before the owners should appreciate its full value, and the purchasers have then seemed to be in a tremendous hurry to cut the forest and realize on their investment. The story of the development of the lumber markets of the country, and the distribution of the different timbers in the trade, would be an interesting story by itself. With tremendous capital at their command, and modern methods of logging, the lumbermen have made such great inroads into the forest that many sections are already practically exhausted. It is stimulating to go into a modern sawmill and see the marvelous rapidity with which great logs are manufac-

tured into lumber. In some of our mills from 500 to 800 trees are sawed into lumber in a single day, and these are trees which required from two to three hundred years for growth.

Yet with all this enormous amount of timber used by the people the situation would not be serious were it not for the waste in accomplishing the lumbering, and the loss through fires and insects. In the old days the lumbermen felt little responsibility in the matter of fires. In many cases it mattered little whether a county or a township were burned over as long as the owner's own property was not affected. It was the spirit that in the matter of destruction of forests there was no individual responsibility, and that spirit exists in many parts of the country today. In any new country there is a feverish haste to develop the natural resources, but the development of a country in the American sense has not been true development. It has been the exploitation of the country without regard to the future rather than the development in a constructive sense. At the foundation of forestry is the conception of use, but it is not the old American idea, which has been rather to use up. We have in many parts of the United States tragic examples of the development of the country. Right at our doors southern New Jersey represents a country which was developed. Perhaps some of you know that country. Many parts of Pennsylvania have been developed. Perhaps you know the condition of Pennsylvania. The forest regions of the Lake States have been developed, and the industry which developed them was lumbering. The forests which constituted the greatest natural resource have been largely used up, and the lumbermen who got their wealth and who developed the country, have now gone South and West, leaving the country in many cases desolate and barren. A small part of the timber was actually utilized, a large part wasted, and the land devastated by fire. Today millions of acres of desolate waste bear witness to the American spirit of development. It is safe to say—and I can say it from my own observation—that, except in a few places in the north in the damp country, in certain locations in the high mountains where it is damp, it is very difficult to find five hundred acres together which does not show the effect of fire, where the forest has not

been tremendously injured by fire, and where the present condition of the forest does not show the effects of past fires.

Even when lumbering is not accompanied by fire and insects, the deterioration of the forest is very great. The best individuals are taken out and the crooked and defective trees are left, which the lumbermen do not want. Usually there are left the poorer species to seed up the ground. The soil is often exposed, trees blown over, and at the best the production is very much lowered. But usually there is a certain amount of fire which kills the small timber and seedlings, although it might not affect the old trees. The Government has estimated the average annual increment at about twenty per cent of what it might be. This is probably nearly correct so far as growth in solid cubic feet is concerned. The growth of valuable material is, I believe, not over 10 to 15 per cent of what it might be.

One of the most serious effects of destructive lumbering followed by fires has been the disturbance of river flow and the erosion of the soil. Forest destruction has already caused a damage of many million dollars by silting up navigable rivers and reservoirs, by causing an increase of spring floods and a deficiency of water in the summer, by deposits of debris on agricultural land, by the drying up of the sources of water used for irrigation and for domestic purposes, etc. The value of forests as a protection of water is no longer regarded in this country as a theoretical matter, but the effect of forest destruction on water supply may be measured in dollars and cents and in the aggregate is so large as to constitute one of the principal causes of the present demand in this country for forestry.

You have undoubtedly seen the statement that our virgin supply of timber will be exhausted in about twenty-five years. This statement has been frequently misinterpreted, as meaning that there will be an actual timber famine in twenty-five years. Of course there will not be. It means that our virgin forests will have been largely cut over in twenty-five years. The estimate is made in this way. As nearly as can be determined, the total amount of standing timber in the United States approximates 1,400 billion feet of merchantable timber. Not allowing for annual growth, and assuming the present consumption as 60 billion feet, the supply would be used in less than twenty-five years. Most statisticians assume about 100,000,000,000 feet as the annual consumption, including cord wood, so that it is difficult to see how the supplies can hold out longer than 30 years at the present rate of consumption. You will notice that I have not made any estimate for annual growth of timber, but inasmuch as this estimate concerns our virgin supplies,—trees which are usually from one hundred to three hundred years of age,—and whose growth is probably equalled, if not exceeded, by the loss through decay—we cannot consider very much growth in connection with these old trees. The statement about the timber famine in 25 years

means this: That the class of timber which we are using now will be very largely exhausted in that time. We are using trees for lumber—construction lumber—which for the most part are 150 and more years of age. In 25 years we are going to have very little of that timber left. We are going to use smaller timber; we are going to use trees from 75 to 100 years old; and in some cases trees 40 to 80 years old. In other words, our virgin supplies will have been largely exhausted and we will be using what is now called "second growth," which in many cases is considered to have almost no value.

There is going to be a change in the lumber business, and there will be a gradual adjustment to these new conditions. That adjustment, of course, is not going to occur without some embarrassment to some people. But I am sanguine enough to believe that the American people will wake up to the necessity for forestry pretty soon, so that we may count on a very much increased growth and increment of our forests.

Referring to special trades, perhaps the paper trade is one which is being embarrassed by the scarcity of timber as much as any other, particularly that portion which handles the spruce and poplar of the north. Stumpage is constantly going up. Paper companies in many cases are holding very carefully the lands which have already been cut over, even those which have been cleared. They are even buying second growth poplar and spruce lands with a view to future growth. Some of the big paper companies are already beginning to practice forestry, and it is becoming more and more clear to them that it is not a question of whether they can afford to practice forestry, but whether they can afford *not* to practice forestry.

The tanning industry has its problem of forestry—the problem of securing raw material. It is my understanding that about two-thirds of the bark used in the tanning industry comes from hemlock. In 1900 it was estimated that the stumpage of hemlock was about one hundred billion feet, while our annual consumption now for lumber and all purposes is 3½ billion feet. This refers to our eastern hemlock. The exhaustion of hemlock in the near future is, therefore, a problem for the tanners. It is probable that the estimate made in 1900 was pretty conservative. This will include only the large holdings. There are many small bodies of hemlock which would not be included in this estimate and which probably would not be of any interest to tanners because from such scattered sources it probably would not be profitable to gather the bark. Unfortunately the hemlock is an exceedingly slow growing tree, although it could be made to grow very much more rapidly than in the virgin forest.

Chestnut oak is located chiefly in the southern mountains. In some sections the accessible timber has been very largely cut. I understand in some instances red oak and yellow oak are being utilized to eke out the supply where the chestnut oak has been exhausted. Our chestnut

has a very wide distribution and there are still very large quantities left, but the original timber is being cut rapidly at a rate of something like 400 million feet a year. The chestnut oak is an exceedingly slow growing tree. It does not grow rapidly anywhere, but its common occurrence is on dry, rocky ridges and slopes where the conditions are unfavorable to rapid growth of any tree. I happen to own myself some forest lands in Pennsylvania, where the chief timber is chestnut and chestnut oak. During the past summer I made a study of the growth of these trees. On an average it takes 80 years to produce a chestnut oak tree 8 inchs in diameter 45 feet high. Chestnut grows very much more rapidly. Some of you may feel that this problem does not concern you very closely. for the use of extracts is increasing very rapidly, and such materials as quebracho are being imported for this purpose, and in the Tropics are many other kinds of wood, like mangrove, and the various acacias which yield satisfactory products. Nevertheless everyone must appreciate that it is important to have a domestic supply of bark and extract wood.

Such in general is the problem of American forestry. Like any other problem affecting the general welfare it must be worked out largely through the Federal and State Governments. Trees grow very slowly, as illustrated by the chestnut oak. and forestry as an investment, leaving aside the speculative features, yields at the best a small interest. Forestry requires essentially a permanence of ownership. It is obvious that the average American proprietor will not under the present conditions adopt measures of forestry for the benefit of future generations. The first step in the introduction of forestry in any country is public legislation. Such legislation must provide for a certain amount of public forests maintained in the interests of the public welfare, both from the standpoint of their indirect benefits and their products. The next step is the actual introduction of forest management on the lands. How far have we progressed in these matters in this country?

We have accomplished a great deal in that public interest has been aroused. The attention of the whole country has been called to the need of forestry. We have reached the point where the public is demanding that something be done to prevent the waste which is now going on. and to inaugurate a constructive policy of forestry. While the loss has been deplorable, it is probable that nothing has happened to benefit the forest movement so much as the recent destructive fires which were so extensive and numerous that the smoke from them reached most of the people of the United States. A further important step has also been accomplished, namely, the introduction of a clearly defined federal forest policy. Already 170,000,000 acres of public land have been set aside as national forests, and a conservative policy has been established for the protection and development of these forests in the best interests of the public in the long run. And already the framework of an organization for the carrying out of this work has been

constructed. This forest policy, if properly developed, will lead to the solution of the problem of forestry in our great West. Its influence, although it is of only recent origin, is far reaching, and already touches an immense number of industries. In parts of the West today many industries are immediately dependent on the way in which the national forests are handled, and the more intelligent of those in the direction of these industries recognize that they themselves will be in the long run benefitted by the new method of forestry in contrast to the old. The forest policy of the Government was the forerunner of a policy of much wider scope. The application of the principles which underlie forestry are the same as those at the basis of the conservation of all our national resources, and the movement for the conservation of our waters, of agricultural interests, minerals, and so on, follows directly and is intimately dependent on the conservation of forests. We believe that a great deal has been accomplished in public forestry, but even in national matters the beginning has only just begun. The policy has been established, but the work of carrying out that policy, the work of organizing the forests, the work of operating and developing them, remains yet to be done.

If this work is done properly, substantial appropriations must be allowed by Congress. We are now spending each year only about seven mills per acre for this development work on our national forests. In Prussia, although the expensive work of organization has been entirely finished, there is spent each year about $2.00 per acre, and there is a gross return of about $4.00 per acre. As I say, for protecting from fire, for building roads, telephone lines and all work of organization, we are spending but seven mills per acre.

MR. KERR: For each acre protected?

PROFESSOR GRAVES: For the whole thing.—170 million acres. And in Prussia they spend $2.00 per acre and get back $4.00, making a clear profit of $2.00. They have only 7,000,000 acres, yet they make a clear profit each year of $14,000,000.

MR. KERR: How about taxes and interests?

PROFESSOR GRAVES: The $2.00 is net. While our western forests are mostly in high mountains and will never be as productive as those in Prussia, at the same time the income will be large, so that it will not be altogether outgo for our Government. In fact the income of the national forest already nearly covers the amount spent.

Our federal forests are all situated in the West. The bulk of the forests from which we draw our supply here and the bulk of the most productive forests in the country are in the East. I would except, of course, certain forests on the Pacific Slope, which are in a class by themselves. Our problem, therefore, concerns about 400,000,000 acres of property owned by private individuals, most of whom are not practicing forestry, and the majority of whom probably will not do so. If the Government wishes to control any of this land it must purchase it.

In my judgment this is exactly what the Government ought to do in the case of certain tracts of land which lie on the borders between different states, and the protection and development of which concern the several states in common. The principal problem in the East, however, must be worked out by the individual states, in the majority of which there must ultimately be public land owned and operated by the state. These lands will be held as public reserves for the supply of a certain amount of timber and for the protection of rivers. They will serve also as object lessons to private owners of how land may profitably be handled under forestry methods. Already a beginning has been made in Connecticut, Massachusetts, New York, Pennsylvania, New Jersey, Maryland, Michigan, Wisconsin, Minnesota and California; and within a year or two probably half a dozen other states will have definitely inaugurated this policy.

State legislation is required, however, to assist the private owner to practice forestry. As long as his property is in danger of being burned, and if he is unreasonably taxed, the private owner will not practice forestry, but he will cut his timber and take out its value for investment in some surer security. Legislation has already been introduced in several states, looking to fire protection, but the laws have not been put into practice. Probably a few lessons such as we have recently had will do more than anything else to bring about a reform in this direction. Some forest lands are taxed unreasonably, and it is clear that on a very long investment, as in growing timber, large taxes will entirely eat up profits.

Tariff reform is often advocated as a forest measure. It may be very desirable for many reasons to reduce or do away with taxes on Canadian timber, but this would help forestry only in a small and temporary way. It may help our forests a little to destroy the Canadian forests first, but there is no permanent remedy possible until forestry is introduced both in the United States and into Canada. It is a great deal bigger question than the tariff.

Public legislation is required both for our public lands and for private forestry, but the real solution of the problem lies in the actual management of the forests themselves. Our forests must be protected, utilized and reproduced without waste, and without loss of production. The broken down and ruined forests must be built up, and all this work depends upon the men who have it in charge, in other words, upon the introduction of scientific methods of treating the forests.

I believe that there is a great deal in the present forestry movement of immediate value to those interested in the tanning industry. In the first place we are endeavoring to secure through federal purchase a very large area in the Southern Appalachian Mountains to constitute a National Forest. The purpose of this forest will be not only to protect and conserve the water power, generated in the mountains, but also to produce wood and timber for the use of the people. This

region includes the principal supply of chestnut oak and chestnut of the country and it is also a natural region for the growth of hemlock. Our National Forests in the West contain a large quantity of western hemlock, of value to the tanner. The forest reserves of the State of New York and those being established in Pennsylvania will serve exactly the same purpose. I have no doubt that in the near future we can secure State reserves in other hemlock and oak regions, such as Virginia and West Virginia, and Maryland, in sections outside of the area included in the Federal reserve. Here again there will be a production of timber guaranteed by the State, which cannot be accomplished through private enterprise.

There are many problems connected with the production of timber for these and other purposes, which have to be worked out by the foresters, but whose results affect users of the forest products. Some of these concern methods of production. Others concern the conditions under which the best products can be secured. I do not feel satisfied that sufficient investigations have been made in this country, regarding the age at which the best material for the tanning products can be secured. In Europe the tan bark oak is managed on a short rotation of sprouts. The trees are cut every fifteen to twenty years, the highest percentage of tannin being secured at that age. Such studies as have been made of hemlock in this regard are not conclusive, for they were based on trees of different diameter rather than on trees of different age. You know you may have a 10 inch tree that is 200 years old and a 2 foot tree that is 200 years old. There are not any satisfactory investigations of any of these points, so far as I know, and when it comes to a question of production in the future many of these questions will have to be worked out.

I think that the foresters may justly claim your support, both in the legislation which we are endeavoring to secure in the different States and in Congress, and also in the scientific investigations concerning the production of material used in the arts. We are developing at Yale in connection with our Forest School and the Scientific School, a strong department in forest products. We are working out many of these problems, partly in the laboratory and partly in the field. Doctor Deane, a member of this Association, has charge of the laboratory work. In the Forest School with which I am connected our work has more to do with the practical problems in the field, and we hope in the long run to be able to develop there a department which will be not only useful in developing young men to do the practical work of forestry, but also which will be useful to various trades throughout the country.

There are a number of points which I might have touched upon in this discourse. One was suggested this evening by your President, and that is the disease which has recently attacked our chestnut trees. It is often called an insect trouble. It is a parasitic fungus disease which lives on the tree and is sapping its vitality. This disease has appeared

most seriously in the State of New York, near New York City and up the Hudson, and in many cases it has taken pretty nearly every tree in its path. It has reached Southern New York, in Orange and Sullivan counties and has been reported also in Connecticut and Pennsylvania. The scientists who have worked on it are very pessimistic about it. Some think that our chestnut is going to be wiped out just as a certain peach disease at one time killed all the peaches in certain districts. So this chestnut disease may wipe out the chestnut unless some unforeseen circumstance happens. I can only say about that myself that we do not know any way to stop it. If everybody were able to go out and make a scientific investigation and cut down every tree that was diseased before the fructification of the fungus and the scattering of the spores, which are blown great distances, we might be able to stop it. But that is not practical. I can only say this, however, that I do not know of any parasitic disease that has ever wiped out a forest species. I do not know of any which has ever done any more than local damage. While we cannot see any way to stop this chestnut disease, and we do not see any reason why it should not do an enormous amount of damage, at the same time I do not believe that our chestnut will be wiped out. We are hopeful that some seasonal changes may check it. I have some land myself, which I bought because there was chestnut on it, and I am just as much interested in this in a personal way as a great many others; and I am going to hold onto my land and not cut my trees down until I find the disease actually working in them. I should be very glad indeed if there would be any discussion about these matters, and would be glad to answer any questions.

DISCUSSION.

MR. SMALL: I am sure that we are all deeply indebted to Professor Graves for coming here and giving us this most interesting talk, and as he said, I think he will appreciate it if there is some discussion of his most interesting paper, and questions asked with regard to any points that may interest any one of us. It will seem too bad that we cannot learn all that is possible from him now that we have him here.

PROFESSOR GRAVES: The fires, as of course you know, have been very bad this year. The probabilities are that the damage may be somewhere between 50 and 100 million dollars. Most of the fires have burned on cut-over lands. Most of the fires in Michigan, Wisconsin, and Minnesota I understand have been on cut over lands. The Government has large holdings and have had very little damage from fire until this year, and their damage will be very, very small compared with the rest of the country. They had one severe fire in Oregon in the DeChutes district which burned a good many million feet of timber, but that is the only disastrous fire they have had, although their forests are very much undermanned.

MR. SMALL: The same is true, is it not, of Canada, to a large extent?

PROFESSOR GRAVES: The Canadian forests have not been organized at all, hardly. They own the land—they have done better than we have—but they have a small organization.

MR. SKIDDY: What is considered the greatest cause of these forest fires?

PROFESSOR GRAVES: Railroads, wherever there are railroads. I saw a map the other day of the forest fires this year in the Adirondacks,—just strips along the lines of railroads, and half a dozen splotches of fires in other places away from the railroad.

MR. SKIDDY: Is that the greatest cause?

PROFESSOR GRAVES: The greatest cause. Every locality has its own causes. In the far West lightning sets a great many fires. Probably the original fires were caused mostly by lightning. The Indians set some, but it was mostly lightning. Forest fires are nothing new. Among the California redwoods they find traces of fires sixteen hundred years old, by counting the rings.

MR. KERR: We have the railroad trouble with fires. However, we have a good State law. The railroad is now liable for any damage.

PROFESSOR GRAVES: Does that work? We have those laws up here.

MR. KERR: I do not know how it will work. We haven't tried yet to collect. It is not possible under present conditions for the private individual to use forestry and protect his property,—land which 50 years from now would be worth a certain sum would cost as much or more to hold. We have had considerable trouble this summer, in common with other people with timber lands, with fire, and most of our trouble has arisen from the small clearings. As you said, there are few people who know what a million acres of land means. I am going to drop considerably and say 25,000 acres. We have as many as 40 to 50 clearings, comprising a few acres, and at this season and in the spring these mountaineers will rake up the stuff and they will burn it up, and the wind will whip it up and into the woods it goes. So instead of having the danger of one railroad passing through our property we have forty to fifty places to watch. We would have to have a staff of 150 men if we ever hoped to keep fires out. The particular tract I am talking about now in the last ten years has come down from a lumber proposition to a railroad tie proposition on account of the forest fires. Of course there is some lumber on it, but it would no longer be considered a first class proposition. We are unable to control the fires.

PROFESSOR GRAVES: If you started in with your 25,000 acres now to organize a system of forestry on it, or fire protection, you would of course have to spend considerable money, and would have to develop it gradually, because public sentiment comes very strongly into this question, and in some sections you have to begin with that.

MR. SKIDDY: Take a fire in a forest, when it gets started, is the undergrowth that you will find in many forests more dangerous than the trees themselves? Does that carry the flames?

PROFESSOR GRAVES: Anything inflammable carries the flames. If the bush growth is green it will not, but if there are a lot of dry leaves on it it burns through them. It carries it along pretty fast.

MR. SKIDDY: The lighter stuff will take the flames quicker than the heavier stuff will?

PROFESSOR GRAVES: It is not the object of the forestry to clean out growing undergrowth. It is chiefly the litter that carries the fire.

MR. KERR: The trouble is the fallen timber. Go into an area that has been cleared, you know that the great percentage of wood in a tree is left in the woods. What they carry away for lumber is an insignificant part. It stays on the ground and becomes like match paper. A fire will lie in it, and it is like a slow match. It will pick up a spark and carry it 100 feet. You may throw water on it, stamp it out and go away and come back in fifteen minutes and the fire is there. You cannot tell where it is going to light. It will make jumps,—a puff of wind will come and it will start 20 fires all around you.

PROFESSOR GRAVES: One thing that will be found in the south, if a National Forest is established, is that public sentiment will be improved. The whole public sentiment all through that section is changing regarding fires, and it is a very hopeful sign.

MR. WILSON: How much State land is there in Pennsylvania?

PROFESSOR GRAVES: About eight hundred thousand acres. The last I heard was 900 thousand acres.

MR. WILSON: With regard to the reproduction of hemlock, does it reproduce itself on poor land?

PROFESSOR GRAVES: Not much. Hemlock requires moisture in the air, and you will find it on the north slopes. You will find it on streams, in gullies,—wherever there is a humid air, and you take on a barren slope where it is all dry, it will not start until after the other growth is started, and then it creeps in underneath.

MR. WILSON: A few days ago I was going through a valley, I presume five or six miles long, and the young hemlocks were coming up, it looked by the million. They were coming up right out of old, rotten logs and roots, not yet reaching the earth, but coming right up out of the old logs, and out of the moss.

PROFESSOR GRAVES: In some places in the North woods I have seen almost all of the hemlock growing in rows because it germinated on rotten logs.

MR. KERR: I think there is a mistaken idea as to the amount of hemlock in the South. I have heard a great deal about it but never could find it. It grows, as you say, up in the narrow gorges and gullies about 100 feet wide in a strip. So far as we could see, the prospect of re-forestration of hemlock is pretty slim. In the first place, it grows

too slim, and in the next place, the second growth, so far as we have been able to determine, does not have the same bark growth that the old trees have. The oldest hemlock tree we ever cut was 396 years old. It was four feet, two inches in diameter, and if that tree had grown up in Pennsylvania or Michigan or up here it would have had bark from 3½ to 4 inches thick from inside to outside. As a matter of fact that bark was not an inch and a quarter thick. So you see the age of the tree has nothing to do with its tannin production at all, and the standard production of bark in Pennsylvania some years ago—and I do not suppose the fact has changed—was actually seventeen hundred and fifty feet per acre, of bark. It was always estimated as two thousand feet to the acre, but I took the trouble to measure up thousands of acres under the log rule, and it figured up about 1,750. The same thing in the south, in northeastern Tennessee, southwestern Virginia and North Carolina. The timber in that section takes 4,500 feet to the acre. So you see that the same estimate of stumpage would not mean the same thing down there as it would up here. The fact of the matter is that to anyone who has made a study of the tanning materials of this country the future of hemlock need not be counted on at all. This country will have to depend—is going to depend—for domestic tanning material upon what is grown between the southern country of Pennsylvania and the northern country of Georgia. That is where we will have to depend for our tanning material unless something else is introduced.

PROFESSOR GRAVES: Do you know anything about the western hemlock?

MR. KERR: Oh yes, I know something about it.

PROFESSOR GRAVES: That has a larger percentage of tannin than ours?

MR. KERR: Yes; a much larger of percentage of tannin. I expect that when the facilities of marketing the tannin produced from that timber, on this side of the Rocky Mountains are perfected it will go the same way that Pennsylvania and Michigan have gone. Two weeks ago I was talking to perhaps the largest pine dealers in the south. I talked with them about re-forestrating; in fact I was walking through the woods down there and the long leaf trees were coming up, and I said to one of them, "You can't leave it—the land is not worth fifty cents an acre—you cannot let it grow." They said, "You can have all you want; it will be donated to you if you will sign a contract to pay the taxes." He said, "I wish I could get some one to take this land off our hands." That is their idea of re-forestrating. They are the second generation of lumbermen who have gone through this very experience in Michigan. They made millions up there and went into Mississippi, cleaning up there, working night and day,—anything to get it cut and get away from there and spend the money somewhere else.

MR. WILSON: Exactly the same thing in Pennsylvania.

MR. KERR: If anyone wants a farm in the Gulf States I will guarantee to get it for them if they will pay the taxes. They are giving

the land away. Now, we have been studying the question of re-forestration in connection with our chestnut timber for the last 7 or 8 years. We have been watching it very closely. We find that while we have not been able to get any definite figures as to interest, taxes, depreciation and what it would cost to protect against fire, we have been going on the blind hope that nothing would happen. We are cutting on the same land that we are endeavoring to re-forestrate. At the same time we feel we cannot go on indefinitely without some assistance from the Government. We have been in very close touch with the Bureau in Washington for years and years and they have discoursed to us and given us all kinds of jollies about what a fine thing it is. We know that too, but they do not start right, unless they mean by this popular agitation to arouse the people to get after the legislation through State or Federal laws, I don't know which. The only way they are ever going to succeed is to relieve the individual of the burden of taxation.

PROFESSOR GRAVES: That will have to be done through the legislature.

MR. KERR: Chestnut timber for our purpose will reproduce itself to make a profitable cut, and take it, all in all, I do not know but what it is a good investment, provided we have a reasonable assurance that in twenty-five years there will be something to cut. The constant recurrence of those fires that comes over the mountains every year kills anything like chestnut that would grow.

PROFESSOR GRAVES: Chestnut is pretty sensitive to fire. We have a great deal of chestnut in Connecticut and we have made a great deal of study of that.

MR. KERR: I think the chestnut up here is more tender than ours. You scald a young chestnut and it is done for. It does not have to be burned even,—maybe charred, the outside of the bark, but the tree does not necessarily have to be burned like an old tree where you can burn half of it and it will keep on growing.

PROFESSOR GRAVES: Of course in the old tree the cork in the bark acts as a non-conductor.

MR. KERR: Perhaps you have often done it yourself—camped out at night and built a fire alongside a big tree and burned a hole in the tree and it would not kill it. But if you take a young sapling and built the fire close enough to it it vaporizes the moisture—a young chestnut tree growing like that will contain in the neighborhood of 60 per cent of water, and you heat that up, and as I say, it blisters the bark off. You can go around afterwards and push the bark in with your thumb against the sapling. It will kill the tree. That may not be the case up here.

PROFESSOR GRAVES: I think they are just as sensitive, but we don't have so many fires.

MR. KERR: Our population is all right, but so far as putting a fire out, it doesn't care to do that.

MR. M. L. GRIFFIN: I am very much interested in what Professor Graves said this evening. I think very often of the extravagance in the wood business, with all that goes between the two ends. It seems to me that the paper industry will, one of these days, make a great deal of valuable material out of a lot of stuff which they ignorantly waste now, and I would not wonder if that was more or less true with people who are making extract and burning up the wood afterwards. What Professor Graves has said about the paper business and the re-forestration is obvious. The large paper concerns are doing something at re-forestrating some of the lands. The West Virginia Paper Company in Virginia are buying a large number of seedlings every year and they have told me recently that where they are cutting they are getting very rapid growth from some of their lands in West Virginia. And they must continue to do that. At the same time they are the most extravagant consumers of wood, and the American people are quite as extravagant in buying the Sunday papers which use up so much wood. I wonder if there are other sources of available tanning material besides those which have been mentioned this evening in any quantity, including chestnut oak and hemlock.

MR. KERR: There is twice as much chestnut growing in this country annually—this is some of our own estimating—it did not come from the bureau—as would be enough to tan twice the number of hides that are tanned in this country today, and that could all be preserved. It won't—but even suppose half of the timber country today is destroyed, there will still be enough chestnut wood to more than tan every piece of leather that can be used.

MR. GRIFFIN: I wonder if there are not other sources of tanning material that are cheaper than chestnut wood.

MR. KERR: It is pretty cheap.

MR. GRIFFIN: Are these the only sources that are in sight?

MR. KERR: Unless the paper man can develop the waste sulphite liquors. I am sure the paper business would be only too glad to try it at any time you can show them.

MR. GRIFFIN: It is a question of pollution; not a question of making money out of it. The paper people were driven out of the Potomac River country on that account. It is a very serious matter for the paper makers—the pollution of streams, and that is the only thing they care about. There is a man in New York who has threatened to prosecute every paper mill in northern New York. He will probably not do it. The State of Tennessee has already gotten after one sulphite mill, and they would be very glad to furnish the leather people all they want.

ABSTRACTS.

The Economical Side of Tan Analysis. R. R. *Gerber*, 1908 [34], No. 819, p. 278.—This is a plea for rigid uniformity in the methods of commercial analysis. So long as the use of more than one method is recognized, the dealer is bound to rate his product by the method giving the best figures.

The Future Operations of the I. A. L. T. C. ALFRED SEYMOUR JONES. *Collegium*, 1908, No. 330, pp. 398-9.—The author suggests (at the Brussels meeting), now that tannin analysis has been sufficiently concentrated upon, that various commissions be appointed to investigate other equally important problems and as a particular subject proposes a rational system of preservation, cure and disinfection of hides, skins, etc.

A New Grade of Gambier Extract. J. PAESSLER. *Gerber Zeitung*, 1908 [51], Nos. 272-4—Gambier ordinarily comes into commerce in two forms, a pasty extract (block gambier) and a solid extract. The native source is from the Malayan peninsula and islands where the leaves and stems of the plant are extracted in a very primitive fashion, giving a product of variable composition often containing much refuse. In recent years an extract factory has been erected in Sumatra operating according to the most approved modern methods, vacuum concentration, etc. The product is known as Indragiri Gambier and has been lately examined in the Freiberg station with the following results.

	Indragiri Gambier		Average ordinary block. Gambier		Impure block. Gambier	
	Filter	Shake	Filter	Shake	Filter	Shake
Tans	42.4	30.2	39.0	27.0	39.8	27.7
Soluble non-tans	17.4	29.6	13.0	25.0	9.2	21.3
Insoluble	3.4	3.4	8.0	8.0	14.7	14.7

The differences by the shake and filter method are very pronounced in gambier because the catechin there present is not taken up by hide during shaking. The Indragiri gambier is seen by the analysis to be superior; it is nearly free from insoluble material which is convenient for the direct preparation of liquors. It is about 3 per cent. richer in tan than ordinary gambier. The non-tans seem to be higher; perhaps the manufacture may be modified to overcome this and increase the ratio of tans. The new extract behaves well in the preparation of concentrated solutions. The following results were obtained in determining solubilities according to the author's method abstracted in the *JOURNAL*, 1908, [3], No. 11, p. 358.

Concentration	1		2		3		4	
Specific gravity	1.0075		1.018		1.038		1.056	
Grade Baumé	1.1		2.6		5.4		7.8	
	F.	S.	F.	S.	F.	S.	F.	S.
Per cent. soluble tans....	43.5	31.3	42.9	30.7	44.3	32.1	43.5	31.3
Per cent. tans utilized ...	102.6	103.6	101.2	101.7	104.5	106.3	102.6	103.6

This shows no loss by separation of difficult soluble tans even at 8° B. Even higher amounts were found in the liquors than in the analysis showing

increased solubility. Trials in tanning calf-skin with the new extract gave a clear uniform leather of brighter and purer color than with ordinary gambier.

The Action of the Pseudo Bark-Beetle on Pine Bark. W. EITNER. *Gerber*, 1908 [34], No. 819, pp. 277.—This beetle (*Stephanopachus substriatus Payk*) although related to the ordinary bark-beetle differs in its mode of life. The eggs are laid in the interior of the bark, hatch out in the spring and the larvae consume the entire interior bark. The author examined the borings left by these. Microscopic inspection showed that the starch of the bark had disappeared forming apparently the nutriment of the larvae. Analysis showed that the tan stuffs had been excreted unchanged.

	Original bark	Borings
Tans	12.8	17.96
Non-tans	14.9	10.92

The tan-stuffs were apparently unchanged in character after digestion by the larvae for the amount of permanganate required for oxidation was found to be the same. A practical experiment in tanning with a liquor made from the borings showed a normal leather, bright in color, but stiffer than ordinary pine leather showing a lean tannage explained by the absence of the coloring tans. The liquors were not sour, even after addition of a ferment, showing that the material nourishing the acid fermentation had been removed.

The Study of Hide and Tanning. DR. ABT. *La Halle aux Cuirs*, 1908 [52], Nos. 47-8, pp. 755, 772.—In this address the lecturer after an extended outline of the principles and operations of tannin deals with the nature of leather itself. Compared with hide, leather has lost in resistance according as the hide has taken up foreign substances. Alum tanned leather has the greatest resistance, then chrome tanned leather and least of all vegetable tanned leather. The leather from sulphited extracts is brittle which has been mistakenly attributed to free sulphuric acid, but this is not found by analysis. The lack of resistance is due to the supertannage. The study of the operations preparatory to tanning is complicated, fermentation playing an important part throughout the processes of soaking, depilation and bating and is yet but little understood. Other fields of study are pointed out, such as the plumping of hide, the fermentation of tans in liquors, the chemistry of the chrome processes, the study of the fats used in tanning, etc.

School of the Tanner (continued); Depilation. A. SCHMIDT. *Le Cuir*, 1908 [1], No. 13, pp. 5-7.—Arsenious sulphide (orpiment) is used like sulphide of soda to shorten the liming process with increase of rendement. It is particularly used for small hides, goat, kid, lamb, calf, etc., but is too expensive for heavy leathers. Its principal advantage is in giving a soft grain. Unlike sodium sulphide, arsenious sulphide is insoluble in water, and cannot be used without lime as is sometimes done with the former. Authorities are not fully agreed upon the chemistry of its action, but most hold that calcium sulphydrate is the active body.

Depilation by Sweating.—The ancient manufacture of "*cuir fort*" in France is based upon this process; as the consumption of this style of leather

for military shoes is diminishing, the sweating process is also less employed. The method has merits, notwithstanding the errors formerly made when the hides were placed in a moist, luke-warm chamber. The result was a loosening of the hair, but the hide was also in part gelatinized and damaged. It appears that two fermentations take place in this process; the first useful, attacking the hair sheaths, producing NH_3 which has a solvent action; the second injurious, attacking the hide. Practice has shown that by operating at a cool temperature rather than at 20 to 25°, the action may be regulated and limited to the first phase. The advantage of this process when rationally carried out, compared with lime or sulphides, is that the interior of the hide is not attacked, giving superior rendement. It is erroneous to compare the white weights directly, by liming and sweating; the last will be less but the deficiency in water is re-established in the tannage. The advantages of the sweating process are over-balanced however by the inferior grain produced; the surface is roughened and does not permit the finishing required by fashion.

Frauds in Crude Hides. (Continued). A. SCHMIDT. *Le Cuir*, 1908 [1], Nos. Nos. 11, 12; pp. 17-88, 13-14.—The third method of control, determination of the white weight, is much employed although not always rationally. It is necessary that all operations preceding the weighing be made uniformly for comparisons. The weighing may be made at various stages of the processes after issuing from the limes, but the most certain method is to take the weight after completing the hand work and when the hides have reabsorbed their normal content of water. The greatest regularity is attained by leaving them in water at a uniform temperature over night and draining 2 hours on the horse in the morning. The rendement should then be 78 per cent. Fourteen kilos of glue stock per 100 kilos of raw fresh hide represents the loss by fleshing. Many factors affect the rendement in white weight, variety of the animal, length of the hair, state of preservation of the hide, manner used in skinning, manner of soaking and liming, temperature of water, etc. According to Dr. Paessler, the weight of horns, hoof and tail average 9 per cent. weight of crude hide. The rendement (white weight) of hides dehaired by sweating is appreciably less than by liming, 88 to 100.

Manufacture of Polishing Leather. W. EITNER. *Gerber*, 1908 [34], No. 818, pp. 263-4.—Polishing leather is made in two styles, a chamois leather of soft texture, generally from buffalo hide, used for polishing articles of gold, silver, etc., and a bark tanned leather from walrus hide, used by makers of cutlery, etc. Unlike most bark tanned leathers, the requisite is a spongy texture; walrus hide already possesses this, being thick and impregnated with fat. These hides are generally marketed in the dry state, weighing about 200 kg. apiece and having 2½ sq. metres surface require a special soaking. Because of their fatty nature, the limes are "sharpened" with 3 kg. sodium sulphide to the hecto liter. The oil becomes emulsified and is partly worked out on the beam, and the hides are then transferred to a bath of 1 per cent. sulphide at 30° C, remaining 2 days. They are again worked on the beam and then go to an old lime, remaining 10 days, are then dehaired and put in a fresh lime for 8 days. Here they swell excessively,

which is desirable for this brand of leather. The large amount of lime thus taken up is removed with HCl and after washing the tannage is begun with a weak acid liquor, pine being very suitable. The hides remain 2 days in each of the 8 vats of the series. On account of their unusual length, the hides must either be suspended by the middle over poles or else simply laid in and daily turned. If the plumping is not sufficient, HCl is added. From the sour vats, the hides then go to the sweet liquors in a series of 20 vats, the last not exceeding 25° barkometer. Here easy penetrating tans should be used, such as a clear settled solution of mixed quebracho and chestnut extracts, also liquor direct from oak-bark, or a mixture of 70 parts pine-bark and 30 parts quebracho. Further addition of dividivi, algarobilla or mallet may be made. The tannage is finished in layaway vats, the first having the same liquor as above. For dusting, oak-bark, pine-bark or quebracho with addition of 20 per cent. galls or 15 per cent. myrabolams and 5 per cent. valonia is used; the first layer stands 4 weeks. The second has a strength of 30° prepared by strengthening an earlier liquor with pure quebracho; dusting material the same, but the hides remain here 6 weeks. The third layer is strengthened to 35° with quebracho; for dusting, a mixture of 2 parts tan-bark, 1 part myrabolams and 1 part valonia, hides remaining 4 months. With thick hides, a fourth layer is necessary. The hides are then washed with luke-warm water and lightened in a sumac bath, 5 kg. Sicilian sumac to a hide, entering at 35° C, remaining 5 hours; they are then turned, the bath again warmed to 35° and the hides left over night. After draining, they are oiled upon both sides with whale oil and air dried. To avoid mildew spots from the sumac during the long drying, there should be good ventilation. Only at the close may the air be heated, 30° C at the highest. Currying is not needed and would be difficult.

Because of the scarcity of walrus hides, buffalo hides are employed as a substitute. They naturally yield a leather of spongy texture which is here increased by the special process. The hides (best from Singapore or Batavia) are softened in 4 per cent. sod. sulphide 6 to 8 days, when they become much swollen and may be fleshed. They are then placed 3 weeks in pure lime which is renewed every week; here they become very thick. After dehairing, deliming with HCl and watering they shrink again. The tanning begins in acid liquors, best pine, in which the hides must be swelled again; if the acid is insufficient, formic acid must be added. Next follow the sweet liquor vats charged with clear settled liquors from equal parts quebracho and chestnut extracts. Eight to 12 vats are used, the upper being of 30° barkometer. Every third day the hides are shifted. The further tanning is also carried out in layaways, the first with 35° extract liquor, quebracho and chestnut and dusted with pine-bark and myrabolams, 3 to 1. After 4 weeks, the hides go into the second vat of 40° remaining 6 weeks. The tanning is finally completed in a Japonica solution with daily warming to 24° C for a week or else in sumac as above.

Glazed Chrome Leather, A. SCHMIDT. *Le Cuir*, 1908 [1], No. 13, pp. 27-8.—This is fully equal to glazed leather from vegetable tannage and in some respects superior. This is principally due to its receiving the glaze on

the grain and not on the flesh. When vegetable tanned leather is glazed on the grain, it is necessary to remove the surface in order that the ground may penetrate and attach to the fibers. Each coat of ground after drying must be pumiced by hand and together with the final glaze forms so thick a layer as to reduce the suppleness of the leather. It is quite otherwise with chrome leather; here the glaze is applied direct to the grain and the less the better. It is only necessary to apply several coats of dressing and a single thin coat of glaze, which scarcely penetrates and does not mask the grain structure. Calf glazed on the flesh has much less the appearance of genuine leather than the glazed grain of chrome leather. Another advantage of the leather is the small amount of material required which permits fine leathers to retain their flexibility.

In order to attain these advantages specified, it is necessary that the manufacture be rationally conducted. The same principles do not govern here as in preparing vegetable tanned leather for glazing. It is particularly important to save the substance of the hide since chrome tanning cannot make up its loss. Soaking in foul water and prolonged treatment with old limes do the most damage. The soaking should be in water often renewed to avoid putrefaction. A good device is to add alkaline substances, especially with dried hides, the process is hastened and some degreasing results. Borax, caustic soda and sulphide are used. Borax is mild but the same effect may be reached with the cheaper caustic used progressively and with moderation. Liming should be short as possible; orpiment and sulphide of soda are used to accelerate, the first being preferred for fine skins. A good method is to use a series of vats, the first strengthened with sulphide of soda or orpiment, and the last containing pure lime. Agitation also hastens the process.

The Manufacture of Patent Leather. *Gerber Zeitung*, 1908 [51], No. 233. —*Boiling of the Lacquer*: 20 k. of linseed oil are boiled 1 hour in a copper kettle at 200° C; then are added 50 g. gold leaf, 1400 g. Paris blue, 400 g. sugar of lead, 300 g. potass. chromate and the whole boiled 15 minutes more at 200°. If sufficiently boiled, the foam becomes black. A better test is to bring a drop on a glass plate and touch with the finger; one should be able to draw out a thread of at least 2 cm. length. The lacquer is then carefully poured off the settlings into tin boxes which are well closed and placed in a warm room to clarify. Several days before use, 1½ k. spirits turpentine are well mixed with 1½ k. of lacquer and a drop tested on the finger nail; It should flow down at once, else more spirits turpentine are added. Then 10 g. fuming sulphuric acid are added with a little spirits turpentine, well stirred in and the whole is then filtered through a layer of cotton resting on a fine wire gauze. It should stand 3 days to clear before using.

Boiling of the Black—20 k. linseed oil and 40 g. gold leaf are boiled 3 hours at 200° C. and then 6 k. ivory black, 600 g. sugar of lead, 200 g. manganese carb., 200 g. Paris blue are added and boiled 20 hours longer. The whole is let cool a little and shaken into tin boxes. Properly boiled, the black should be thick as tar while hot; and draw a thread of 2 inches; when used 1½ k. black are well mixed with 2¼ l. spirits turpentine and ¾ l.

benzine. 300 g. Paris blue are mixed with about 300 g. of the dilute black and about 200 g. spirits turpentine and ground 3 to 4 times in a color mill till the blue is fine grained; then it is well mixed with the remaining black. When of the right consistence, a drop should run off the finger nail held aslant. In use, the mixture should be shaken every 10 minutes.

Boiling of the Ground.—20 k. linseed oil are boiled 6 hours and then 1.2 k. of fresh cut slices of bread are added, continuing the boiling 3 hours, when the bread is removed. Then are slowly added 200 g. umber, 200 g. gold leaf, 200 g. white lead, 800 g. rubber threads, boiling 6 to 8 hours at 260° C. A drop on glass should become thick and sticky and give two or more threads with the finger. The kettle contents are cooled to 150°, and then are well stirred in 800 g. lamp black, 200 g. ivory black, 4.8 k. benzine, 1.6 k. spirits turpentine and when sufficiently cooled all transferred to tin boxes. For use the ground is filtered through gauze and diluted with ½ volume of benzine.

Process—The leather to be properly soft is staked in both directions and then stretched on frames, but not too tense. The ground is slowly applied with a sponge and well rubbed. The frames are placed in the sun to dry and then treated again in the same way. Next it is rubbed with artificial pumice No. 2. While still in the frame, the dust brushed off and the black applied with a broad brush stroking alternately cross and lengthwise. The frames are then placed in the oven, grain up, and dried at 50° to 56° C. for 8 to 10 hours, then stood in the sun or dry air till no longer sticky. The dry leather is removed from the frames, placed on a felt covered table and ground with pumice, then dusted, pebbled in both directions, again framed, washed with cold water, rubbed dry, dusted and lacquered. The lacquering should be done in a room free from dust and draft, the walls and floors being sprinkled before work. A soft broad brush is used, first lengthwise, then across. After drying 15 hours at 62° C. the frames are left in the sun or air till no longer sticky; then the leather is trimmed and lightly polished with window leather.

Split Leather with Imitation Grain. G. E. *Gerber Zeitung*, 1908 [51], No. 232.—In most factories, the hides are split after liming and when watered and bated are tanned in the drum. Some begin with a weak liquor of 3° and gradually strengthen to 7°, others begin with strong liquors. A simple means of hastening the tannage consists in adding a certain amount of oil and several pounds of salt to each new lot going into the drums. The oil prevents heating and renders the leather soft. The salt by its plumping action hastens the absorption of tannin and also reduces the red color so frequent in drum tanning; an excess should be avoided which prevents drying and raises the question of intentional weighting. After the drums, it is well to suspend the splits a short time in strong liquors. Simple washing gives a strong merchantable leather.

To produce the imitation grain, the splits are washed after tanning in a weak borax solution. If to be dyed an additional washing with weak H_2SO_4 in the drum is advisable. The borax as well as acid should be thoroughly washed out with cold water. The leather is then milled two hours with a

fat liquor made from 2 parts Marseille soap, 1 part bone oil with addition of some soda and then hung up over night. The next morning they are stroked on both sides, oiled on the right side with linseed oil and dried. Before dyeing, a light bleaching is well; aniline or vegetable dyes are used, generally black or chocolate brown. After dyeing, the finish is applied to take the grain; a solution of flaxseed in warm glue or gelatine solution is applied to the dyed surface and after drying the desired grain is impressed with the roll. Finally a lac finish is applied to fix the grain and make it waterproof; it consists of wax and a solution of rosin in spirits turpentine. With careful preparation, the product is scarcely distinguishable in appearance from grain leather although naturally less durable.

The Tanning of Kangaroo Leather. *Gerber Zeitung*, 1908 [51], No. 246.—Before liming, a thorough softening and watering is necessary. Chrome tannage gives good leather; for vegetable tanning, gambier or palmetto are employed, also quebracho. Liming is carried out as with goat skins; by the use of red arsenic, hide substance may be saved. After dehairing, the hides are bated with pigeon dung or lactic acid and then pickled with H_2SO_4 and NaCl, 2 to 3 hours with agitation, and then drained over night. In chrome tanning the two-bath process is used and a light vegetable after tannage is of advantage, using gambier or palmetto extracts. For greasing, a mixture of soap, bone oil, olive oil, glycerine and egg yolk is best. After the first greasing, the leather is washed, drained a few hours and then treated in a second mixture of 1 part bone oil, 2 parts paraffine and dried at a rather high temperature. The hides are next drawn 3 to 4 minutes through hot water and laid in moist saw-dust. To complete the drying, they are stretched on frames; while drying the outer side of the leather is rubbed thoroughly with a solution of lactic acid. When dried, re-stretched and polished, they are treated with a dressing made from ammonia, glycerine and logwood extract.

Greasing and After Tannage of Upper Leather which has Become Hard, in One Operation. *Gerber Zeitung*, 1908 [51], No. 240.—The usual process of softening such leather consists in oiling followed by mechanical treatment. In general the leather is milled in warm water till soft, then dried, greased and curried as needed. This is not sufficient however with a very firm leather or when the tanning has been unsatisfactory, when the following process is used: Two to five per cent. of a cheap grade of tannin is dissolved in alcohol and added to the fat to be used. To promote an intimate emulsion, it is well to use some degras in the fat employed. The tannin penetrates well and no further washing is needed. The process is not suited for heavy leather.

Employment of Oxalic Acid in Tanning and Dyeing Leather. Czenstochan Chemical Factory, HENRY R. SACHS (pamphlet), through *Gerber Zeitung*, 1908 [51], Nos. 241, 244, 254.—By the use of tropical tanning materials and concentrated extracts, tanning processes have become much shortened. Owing however to the lack of ingredients (sugar) which produce acids in liquors from such tanning materials, the hides are not sufficiently plumped, and a brittle, light weight leather results. Acids must be added to over-

come this and oxalic acid is the best; it is taken up more rapidly than acetic, lactic or hydrochloric acid and only equalled in this respect by sulphuric acid which is injurious. Dr. Paessler likewise showed that oxalic acid was absorbed in larger amount than any other acid except hydrochloric which is also an objectionable acid. Unlike mineral acids which should be used in a separate plumping bath, oxalic acid may be added directly to the to the tanning liquor. As the plumping action is not increased beyond a concentration of 0.4 per cent., it may be used economically. The amount to be added must be determined by the tanner. It is important to add gradually, observing the effect of each addition; if too large an amount be added at once, a rapid plumping ensues, followed later by a shrinkage of the hide which cannot be made good again but produces a rough, soft leather. The plumping should proceed gradually until leaving the handlers, when a later shrinking need no longer be feared. The hide will then be tanned considerably beneath the grain and will finish rapidly in the layaways.

In dyeing leather, oxalic acid is used to fix the dye and vivify its hue. The hides are mordanted with dilute (1 per cent.) solution which is preferable to sulphuric acid which gives a brittle leather. The hides previously softened in water are (after draining) agitated 15 minutes alternately in the acid bath and fresh water as often as necessary to give the desired bleaching. In dying light fashionable shades, also light russet leather, sugar of lead is needed in addition to give sufficient bleaching. The hides softened in warm water are reeled in succession through 3 vats containing respectively oxalic acid, sugar of lead and pure water. A second or even a third stronger bleach applied in the same way follows, according to the effect desired. After the last treatment with water, the hides are again placed in pure water and 50 cc. of conc. solution of water soluble blue (10 grms. to liter) are added drop by drop, until the desired bluish white tinge is given to the leather.

Oxalic Acid in the Currying of Heavy Leather. *Gerber Zeitung*, 1908 [51], Nos. 257-258.—By the aid of this acid, the objectionable dark color given to sole, vache, harness and other leathers by the new rapid processes with tropical tanning materials and conc. extracts can be considerably bleached.

(*a*) *Process with Oxalic Acid.*—Three like vessels of a size to take 3 to 6 hides are set close together and arranged for rapid emptying. The first is charged with a 4 per cent. solution of calcined soda, the second with 4 per cent. oxalic acid and the third with pure water. The alkaline bath is heated to 55-60°C., and the dried leather entered, allowing the liquid to first act on the thicker parts to avoid spotting. After 5 minutes the hides are taken out quickly, drained and drawn rapidly through the third vessel and then placed in the second (acid) bath with the same care as in the first, remaining here also 5 minutes. After rinsing in the third bath, the hides are drained on a horse. Brittle leather need not be feared with good rinsing. After hanging some time, the hides are flattened on the table and lightly oiled with linseed oil.

(*b*) *Process with Salt of Sorrel.*—This is the same in principle, being milder and used with lighter and more sensitive leather. Three baths are likewise used, the first containing 6 per cent. ammonia soda, the second 4½

per cent. salt of sorrel aud 6 per cent. HCl, the third water. The hides remain in the first bath 10 minutes, are then quickly rinsed and laid in the second bath 5 to 10 minutes, again rinsed and finally drained.

These processes should be carried through rapidly and to prepare the bath accurately it is of advantage to use concentrated stock solutions of known standard

Discussion Relating to Large Liming and Tanning Vats (continued). *Gerber Zeitung*, 1908 [51], Nos. 234, 238, 243, 245, 250.—As with limes, the hides should not be turned in tanning but remain always under liquor or in motion. Agitation shortens the time of tanning and is economical. Cement construction is best. By a new process, the hides remain in the vats until completed, the liquors being changed by pumps. Two laborers can thus introduce an unlimited number of hides into the vats and remove them with minimum expenditure of labor. The process is said to give a superior grain and enables filling with extracts to the maximum desired.

No. 238.—Writer thinks it better to move the hides than liquors, the tannage being favored more. If the liquors remain in the same vat, the strong liquors finally condense tan-stuff on the outer surface of the leather preventing penetration. In the drum on the contrary the motion enables the hide to be rapidly penetrated. A heavy hide properly fore-tanned is tanned through in the drum in 36-40 hours and does not need the filling above referred to. If increased weight is required, the drum tanning may be followed by 14 days in the layaways.

No. 243.—This much discussed question cannot well be answered the same for all; much depends upon the nature of the work. As to dimensions, large hides for soles require 2.3 metres breadth, while for vache leather 2 m. suffice. In any case however no portion of the vats should be unused leaving dead liquor, as for example when they are too deep. If hung doubled over poles, a depth of 1.6 to 1.8 m. is enough; when hung by the hind hoofs, 2.5 to 3.2 m. are needed. Writer believes vat tannage gives better leather than drums and that the rendement is not inferior, losses by washing being less.

No. 245.—Tanning in the drum can easily cause irregular folds in the leather, which is partly the cause of the adoption of the filling process. The excess of extract absorbed in the drum is not fixed to the hide but is removed again in the layaways and lower yield.

No. 250.—This writer meets with none of the difficulties last referred to and makes good leather with extracts only in the drum. The principal causes of failure in drum tannage are use of unsuitable extracts, poor form of drums (Grebestein's are best), unsuitable temperature, insufficient fore tannage and imperfect plumping because a suitable series of vats has not been used, and most important of all, faults in liming and de-liming. The trouble in rapid tannage is not with the drum itself, but lack of attention to the processes preceding it. Possibly something may be done in these days with tanning with extracts in vacuo. Writer took part in the work done at he tannery of Daniel Kampffmeyer, Berlin, 1862. Good sole-leather was

produced by tanning 5 weeks in 3 layaways with oak bark and sour liquor; the air was pumped out of the hermetically closed iron vats.

Vanadine Black. *Gerber Zeitung*, 1908 [51], No. 246.—A prominent chemical manufacturer writes to the editor that the recipe for this black (abstract, (JOURNAL, 1908 [3], No. 11, p. 371) originally due to an observation of Berzelius, has an undeserved place in the handbooks. It is not light proof, becoming greenish brown, or gray green when logwood is employed. Its reputation by name is partly due to the occasional use of vanadate of ammonia in the preparation of the durable aniline black from aniline and chromic acid.

Cleansing Drums and Oil Casks from Fat. *Gerber Zeitung*, 1908 [51], No. 253.—These are lightly brushed out with a strong hot soda solution and then completely filled with a dilute solution of same and left stand one day. After emptying, the vessels are rinsed first with hot, then cold water. Freshly dissolved lime can be used in place of the soda.

Water Proof Leather Dressing. (Same).—Four parts castor oil or whale oil are heated with 2 parts tallow in a cast iron kettle to 125° C. and stirred with a wooden paddle to complete solution. Book printer's black may be added to give a black.

PATENTS.

Flexible Roll for Leather Splitting Machines. U. S. Patent No. 905,111. J. J. STEHLING AND F. BRENNER, Milwaukee, Wis.

Leather Rolling Machine. U. S. Patent No. 906,329. W. H. STIMPSON AND F. A. BRADFORD, Boston Mass.

Vacuum Evaporator. U. S. Patent No. 906,517. J. E. and F. M. DUNN, Santiago, Cuba.

Compound for Tanning Hides. U. S. Patent No. 907,060. G. W. LANGLEY, Greenbrier, Ark. A tanning compound consisting of extract of horse-chestnut, extract of poke-root, gambier and water.

Substitute for Patent Leather. U. S. Patent No. 907,087. S. NATHAN, New York. A woven cotton body, having the interstices filled with a gelatinous substance. The treated fabric then receives a plurality of coatings of "daub" similar to the "daub" used in making patent leather, being baked between the applications of each coat of "daub".

Evaporator. U. S. Patent No. 907,109. O. FALLER. Basel, Switzerland.

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The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL . . Past Presidents

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C. W. NORRIS, New York.

ELECTIONS

The following have been elected members of this Association:

ACTIVE

George W. Miles, 29 Central Street, Boston, Mass.
Dr. Stephen P. Sharples, 26 Broad Street, Boston, Mass.
Roy H. Wisdom, 185 North Street, Stamford, Conn.
Frederick R. Hall, Bluff City, Giles Co., Va., care of New River Tannery.

ASSOCIATE

Warren S. Loud, Rear 208 Summer Street, Boston, Mass.
S. D. Eisendrath, 22 Fifth Avenue, Chicago, Ill.
Kullman, Salz & Co., Benicia, Cal.

COUNCIL PROCEEDINGS.

A meeting held Dec. 30th, 1908. Present—Messrs. Wilson, Small, Eachus and Reed.

Analysis of Chrome Liquors.—Decided that before undertaking further work along the line of chemistry of chrome tanning, the secretary learn whether the industry desires our co-operation.

Detection of Ingredients in Tanning Materials.—Decided to continue committee investigation with Mr. Small as chairman, and that the chairman be permitted to select his own committee. Suggestion of Griffith of investigating distillation products referred to Committee.

Soluble Solids Filtration.—Decided not to investigate a centrifugal method of separating the insolubles, that the difficulty with the asbestos-kaolin method is one of manipulation and lack of experience, that care should be observed in preparation of asbestos, which should be of suitable texture. Mr. Small appointed as chairman of committee for ensuing year with power to ask every member of the Association to collaborate in the work as a means of definitely deciding the value of the asbestos-kaolin method.

Color Valuation of Tanning Materials.—Decided that the 1908 Committee should serve this year, Mr. Kerr being reappointed as chairman. Especial attention is requested to the advantage of cow grain splits, and chairman is requested to obtain from Messrs. Small and Alsop methods of preparing and using this skin. Chairman also requested to ascertain effect of boro-phenol solution on resulting color test when not entirely removed from skin by washing. Suggestion of Reed for use of cloth instead of skin and chairman's own suggestion of use of photometer is referred to committee.

Acidity of Tan Liquors.—Decided to appoint Mr. Alsop as chairman of committee, with power to call upon the entire Association for collaboration in order to decide, if possible, whether the Alcoholic-Gelatine-Hematine Method should be adopted. Basic Dye Method also referred to Committee.

Acids, Natural and Artificial.—Mr. Wilson appointed chairman of committee, with Messrs. Tucker, Maxwell and Ober-

fell, to ascertain the advantage or otherwise of adding artificial acids, such as lactic, acetic, formic and sulphuric in the tanning process, and as to whether the addition of such acids preserves the tannin by limiting or preventing fermentation.

Leather Analysis.—Decided to reappoint the 1908 committee with Mr. Hoppenstedt as chairman, with power to enlarge committee if chairman deems it advisable. Committee to determine relative values of cochineal, carminic acid and methyl orange as indicators in nitrogen determination, the best method of ascertaining the water-soluble material of leather, and the correct method of reporting content of magnesium sulphate, whether with or without the water of crystallization. Other matters contained in the chairman's report of 1908 left to discretion of committee.

Chroming of Hide Powder.—Mr. Eachus appointed chairman with power to call on all members of the Association for collaboration. Decided that chrome alum has been proved to be equal and probably better than chrome chloride, but that the committee should try the chroming with smaller volume of water against our Official Method. (Ten times the weight of water to weight of hide instead of twenty-five times is advised for trial.)

Rapid Cooling of Tan Solutions.—Referred to same committee as "Chroming of Hide Powder." The effect of rapid cooling to be determined upon non-tannin results as well as soluble solids.

Acidity of Hide Powder.—Referred to "Committee on Chroming of Hide Powder" and "Committee on Rapid Cooling of Tan Solutions," with power to recommend limits of acidity or a definite acidity or further investigation as may be decided.

Committee on Oil Analysis.—Mr. Alsop appointed chairman with power to select other members of the committee, and to undertake such work as may in his estimation seem wisest, but with the recommendation that the method of determining moisture in Degras as suggested by Dr. Levi be given consideration and the proportionate value of petroleum and sulphuric ethers as solvents.

Extraction of Sumac, Myrabolams, Etc.—Recommended that the method proposed by Mr. Eachus by soaking for one hour and extracting in a Teas or Reed extractor with 2000 c.c. of water by condensation and outside collection entirely in from eight to nine hours, be referred to the next annual meeting for adoption as a Provisional Method.

Sampling.—Voted to again recommend to the Association the adoption of the present method as Official, as it failed of the necessary vote to become Official at the last annual meeting.

Commercial Acids.—Referred to the 1908 committee with Mr. Phelan as chairman, with instructions to draw up drafts for Provisional Methods and present them to the Council for the acids investigated with exception of Lactic Acid, which the committee shall make a subject of further investigation. The chairman is granted power to increase the committee if he finds it necessary.

By-Laws.—Decided to change the by-law requiring a two-thirds vote of all the members for the alteration or adoption of methods to read "two-thirds of the members voting."

Other Business.—Mr. Benjamin S. Priest elected as an active member. Price fixed on back issues of Journal at $5.00 per volume when taken by a member.

Secretary instructed to send bound volumes of Journal to date to Dr. J. Gordon Parker, Secretary I. A. L. T. C.

Matter of increasing membership discussed.

Meeting adjourned.

AMERICAN SOLE LEATHER.

By C. A. Brown.

I have been asked to speak to you on the subject of American Sole Leather and its adulteration, etc. While I have spent a large part of my business life in talking about sole leather for many different reasons, I never anticipated attempting seriously to do all the talking and certainly not to more than one listener at a time. I am not in doubt as to the reasons for my being in this present predicament as I am fully aware that

it is due to early indiscretions in trying to inveigle some of the consumers of sole leather into making purchases, with whom some members of your Association of Leather Chemists are now associated. It is one thing to sit into a discussion but quite different to conclude a matter successfully when you know your hearers hold all the trump cards.

I am not in any way qualified to speak of sole leather in a technical way from the tanner's standpoint as, for the most part, my experience in the leather business, particularly the sole leather end, was in finding a market for it and its application to shoe products. For some nine or ten years I have been on the other side of the fence, buying leathers from my old acquaintances and associates and helping produce the finished product, shoes. My general remarks on the subject assigned me will be, therefore, from the point of view of the shoe manufacturer.

For this reason I will divide the sole leather as used in two fields. First, the Hemlock or so-called red leather tannages, made mostly from foreign dry hides of all kinds; and secondly, the so-called Oak and Union tannages made for the most part from domestic, green hides.

Hemlock leather, which is by far the largest field of sole leather production and consumption, goes almost wholly into what may be termed the cheaper class of shoes; that is to say, shoes that retail for $3.00 and under; the Oak and Union leather being used almost exclusively in the so-called fine shoes, selling for $3.50 and upwards, and also almost exclusively in all women's shoes, the exception in the women's line being such shoes as are made for wear in rough country localities by the very poorest class of customers. The very nature of the hemlock leather defines its uses. It is, as a class, of a stiff, hard, coarse-fibred nature, not lending itself readily to the modern Goodyear welt process, and, when so used, as it comes from the tannery, helps to make a stiff, unyielding shoe, unacceptable to the average consumer who is able to buy one of a more flexible and comfortable nature.

The manufacturer buys his whole sole leather by the pound. But there are various leather products produced from it, how-

ever, by special branches of the business and sold to manufacturers in a prepared form, such as counters, box toes, inner soles of various kinds, heels, taps, etc., almost entirely sold by the pair. I know of but one exception in the sole leather field where any of this kind of product is sold by the foot and that by only a few producers in a very small way. I refer to Chrome tanned sole leather used in a very limited way for bottoming specialty and sporting shoes of various styles and kinds.

In producing a satisfactory welted shoe for the consumer today, it must be reasonably flexible and comfortable to the foot and the outer sole, to properly meet the necessities of the Goodyear process, must also be flexible and reasonably mellow to meet the mechanical features in sewing and finishing. The advent of the Goodyear process and its universal adoption, beginning some twenty-five or thirty years ago, brought up new problems to the shoe manufacturer. He immediately found that the Hemlock leathers that had been used for generations were too stiff and hard to use in good sewed shoes. It would not make an inner sole which it was very essential should be extremely flexible and tough-fibred. When he turned to the Oak or Union field, he found it a restricted one and much too high in price and the Union leather tannages at that time and for many years were regarded as too soft, lacking good wearing qualities for use in men's shoes to any extent, the leather being, therefore, consumed almost exclusively in women's shoes or shoes of a lighter nature. The production of Oak leather, however, was largely increased as demands for other Oak leather products, such as belting, etc., increased and some large lines became available to the shoe manufacturer, produced in connection with the manufacture of belting. This leather was sold at a price that was nearer the reach of the manufacturer making medium priced shoes, the demand for which was very largely increased with the growth of the country and the changing taste and demands of the consumers.

It became apparent, however, to the large manufacturer that the Oak and Union leathers would always be produced in rather limited quantities and, because of the amount available and its cost, it could not be used in popular lines of shoes worn by

the million. The adoption of the Goodyear process was increasing all the time, plainly demonstrating that it was the one coming standard method to be followed and that some lower cost leathers must be produced in some way to make it possible to utilize it in such a shoe. Some ten or fifteen years ago, some shoe manufacturers started in to invent methods to make this stiff hemlock leather more flexible by mechanical means, but it was found impossible to do so satisfactorily and then various experimental methods were tried to soften the leather by dipping it in various solutions, washing out or softening up the ingredients in the leather, and then re-rolling, bleaching, and stuffing the leather somewhat with oils, producing what was dubbed in the trade as Yankee Oak. This method was very extensively tried out by the manufacturers. They were seemingly able to take the lower priced Hemlock sole leather in the side; that is, untrimmed; and after removing part of the tannage by these comparatively simple and probably crude means, obtain a changed piece of leather that was a little thicker or plumper than the original, more flexible, but less water-resisting, with a fair amount of wear, but reduced in most cases.

It has been expressed very generally a curious inconsistency that the tanner should bring his leather to market in the most solid possible form, sell it by the pound to shoe manufacturers who immediately proceed to wash out the weight and change over the leather to a point where he would probably have refused to accept it if offered to him in just such a form by the tanner in the first place. After quite an extended period of trying this out, it was gradually demonstrated that the softening of Hemlock leather was not a practical or economical method for the average manufacturer to go into and, at the same time, the tanners of Oak and Union leathers began to produce flexible, lower cost leathers which had sewing qualities to the necessary degree, so to-day only a very few, and they the larger manufacturers, buying Hemlock leather, use a softening or re-tanning process to make this Hemlock leather available for use where the Oak or Union tannages are intended to go. The undoubted reason for the survival of this process among such manufacturers is due largely to the fact that they must have mellow sole leather in large quan-

tities at a popular price and such can only be obtained in the Hemlock field.

Oak and Union leather is marketed almost entirely in the trimmed form, that is, the heads and skirts are cropped off and used for purposes other than for outer soles. The manufacturer of the lower priced shoes must have cheap inner soles, heeling, top pieces, counters, and box toes, in large quantities, and the untrimmed Hemlock leather, as he buys it, produces all these items. It may be questioned, but it would seem as though the methods in the production of Oak and Union leather had gone through very great changes where the Hemlock product is very little different if any in its appearance and texture from what it was a generation ago.

Because of its cost, Oak sole leather has been necessarily used exclusively in a high priced product. By far the largest field for Union leather has always been in the making of women's shoes, the leather being purchased by "middle men" sole cutters who cut the leather up into a great many different styles, weights and qualities of soles, selling to the manufacturer the particular weight or selection of soles that he demands, a necessity in the production of women's shoes, which are a very different proposition from men's goods. Large quantities of women's shoes are produced by the Turn method (the Turn requiring mellow leather especially) as well as the ordinary welted process.

The leather turned out by the Oak and Union method of tanning produces a fibre particularly adapted for Goodyear inner soles, box toes and counters. The inner sole being the backbone in a Goodyear welt shoe and of the utmost importance, it is essential that this piece of leather be flexible, long fibred and tough, qualities which could not be had in the so-called common Hemlock or dry hide leathers. This is one of the reasons that Oak and Union leathers come almost entirely into market in the trimmed form, the heads being used in the manufacturing of heels and taps, the skirts being worked up into the so-called Goodyear inner soles, box toes and counters. The production of box toes, counters and inner soles is a very extensive and separate branch of the business, large concerns

buying the skirts from the tanner for the production of these shoe supplies, and also purchasing the shoulders from belting manufacturers and others producing sole leather shoulders, for the manufacture of Goodyear welting, rands, heels and similar shoe supplies, to be sold in specialized form to shoe manufacturers.

The inner sole being of so much importance in a shoe, it has a relatively high value and, to quite an extent, this is true of the box toes and counters. Therefore, this brings these by-products of the Oak and Union tannages into so separate and distinct a field and of so great a value that the shoe manufacturer could not afford, neither had he the place, to use Oak and Union leather in the side to use up the by-products to as great advantage as these specialized houses which cut up and sell this kind of material; therefore, the trimmed side in the form of backs is produced. The manufacturer who buys the backs or the cut soles, therefore, is to a great degree dependent upon the separate concerns who make a specialty of producing box toes, counter heels and inner soles for him. He gets specialized just what he wants in quality, texture and price, thereby being able to highly develop his own product and get the maximum of quality and value into any grade of shoe that he elects to make.

While shoe manufacturing was going through such rapid changes and developments in mechanical methods, it is also true that the tanner was departing from the old-fashioned rule of thumb methods and was endeavoring to produce his leathers under greater economies, a benefit to himself and to the public in general. The lower and cheaper classes of leather, most of the Hemlock products, gradually found a very large foreign market, particularly England and all through Europe, our leathers for many years now undoubtedly dominating the entire European market.

At periods some foreign sole leathers were imported into this country, due entirely to the fluctuating price of our commodity here, enabling importers to bring over from Australia and Europe shipments of leather but only in very limited quantities for short periods. The kinds of leather, however,

brought into this country were not profitable or satisfactory to the American shoe manufacturer. As has been previously noted, sole leather is sold by the pound and is cut up and figured into the cost of the shoe by the manufacturer on a loss and gain basis. By that is meant that all the different kinds of shoe parts that are produced by the manufacturer from the Sole Leather that he buys are figured at a specific price into the cost of the shoe. For instance, an outer sole of a certain thickness may be figured into a shoe at 30 cents a pair. Long experience has taught the manufacturer that leather of certain kinds, say at 32 cents per lb., will produce a given thickness of outer sole at 30 cents per pair, and he figures the outer sole into the cost of the shoe at this price, but when it comes to buying and cutting leather to produce this figure, he will try to buy his leather so that it will figure him for less. If he succeeds he will make a gain. If he does not succeed and it costs him more, he will make a loss.

The first thing that the American shoe manufacturer found out about foreign sole leather was that it would not figure, or in other words, cut by our methods it cut at a loss as compared with American tannages of similar nature. And the accepted answer to this demonstrated fact was that the leather was too heavy weighing, or that there was a great deal more weight to the square foot in the foreign tanned leathers than in the American tanned leathers. The leathers could be sold comparatively cheap even with all the necessary charges for bringing it into the country, but it was never profitable because it simply would not cut to figures against American leather and methods. I presume that our tanners as they progressed became familiar with the make-up of foreign products. It has apparently been accepted for years through the trade that the English or foreign tanner was a past-master at weighting and adulterating his leathers and this was the one fundamental reason for his being able to sell as cheaply as he did at the price per pound.

It is doubtful as a matter of fact, if the shoe manufacturer from a technical leather standpoint has ever known or apparently cared very much about the methods of tanning the leather

that he uses. This was natural because of the great variety of processes and numerous complications involved in making leather. All the shoe manufacturer cared about was the results obtained in the finished shoe. In the meantime, the tanners as we have noted were experimenting and developing methods by which to produce leathers cheaper to themselves by making their hides a more efficient vehicle for marketing to the consumer more pounds of so-called leather to the hide than they had ever been able to sell before. The manufacturer of shoes first became conscious of this fact through certain new and puzzling difficulties that he found himself involved with in his finished shoes. Leather kept cutting higher and higher. Counters made from Hemlock shoulders and sides, also from rough splits for cheaper shoes, and from Oak and Union skirting and shoulders, did not seem to have their old time resiliency or stand-up quality in the heel of the shoe. Complaints came forward to the manufacturer that his counters slumped out of shape with wear, they absorbed the moisture of the foot and become soggy and lifeless. This was also true of the box toes, which, if stepped on and jammed, had no recovering qualities and with wear collapsed and fell in and seemed to hold the dampness and sweat of the foot and would not dry out. The inner sole would at times become soggy and the outer soles on these shoes, although finished in the usual way, would cause the shoes to be returned because a bloom or gray-whitish deposit would come out over the highly finished black bottoms. There were appearances in many instances of a white crystallization on the soles after going to a dealer and perhaps kept by him for months. The goods would be returned and the manufacturer would find himself contemplating faulty results that he had never had to meet before.

Changed conditions in the sole leather gradually dawned on the manufacturer and, in looking around for reasons, it transpired that it was due to new tanning methods, the reply being that they were quick or cheap tanning methods. Another answer was that, in order to get a nice white color on the original leather so that it would finish a handsome bottom, bleaching chemicals were used, but the true explanation of it all

was that the tanners had learned to use various new substances not entering strictly into the tanning process, as had the English tanner long before, and purely for stuffing or weighting the leather in order that they might sell to the consumer more pounds of leather, or in other words make greater gains. These difficulties were very serious. The shoe manufacturer did not know how to overcome them. He did not know enough about leather to detect them in the leather at the time of buying. It was a blind problem to him, giving him much trouble and annoyance. Gradually, however, he came to understand cause and effect, made claims for losses, and the tanners woke up to find that their processes were either too crude or that they had gone too far. In most cases where the leather was used for specific and specialty purposes in the shoe, the tanners were obliged to modify their use of foreign substances to a great degree so that now there is less of it used in certain kinds of leathers than there has been although it may also be true that the processes have been so perfected that there may be as much used or more in some kinds of tannages.

Naturally the leathers in which this difficulty appeared to the greatest extent were the cheaper or coarser kinds produced from the coarser and less valuable parts of the hides; for instance, the leather manufactured in tanning the bellies separate from the backs, it being a part of the hide that would lend itself readily to his methods and selling at a low price, he experimented and noted that he could weight more safely the skirts, heads and splits and what might be termed the by-products of sole leather to a very great degree, when he must be much more careful in experimenting or trifling with the backs which produced the outer soles and more valuable parts of the hide the leather from which had to stand severe finishing conditions and produce results that were very carefully scrutinized and apparent to the consumer.

Opinions have often been expressed that the question of weighting leather to such an extent as has been apparently done in this country was first developed by the tanners who were making leather for the export trade; in other words, trying to make leather for the foreign dealer the same way as

had the foreign tanner and in which he was an old hand and expert. The question arises, has the tanner been, by force of foreign competition and the demands of the American manufacturer, obliged to go into a method of over-weighting or adulterating his leather in order to sell it cheaper. The undoubted fact is that weighted leather, or leather produced by what are termed modern, quick or cheap tanning methods, sells for less than pure bark tanned leather produced by the old processes, but this does not say yes to the question.

The shoe manufacturer, as we touched upon in noting the loss and gain method of cutting, is of course continually looking for leather from which he can produce a satisfactory outer sole and, at the same time, give him the greatest degree of profit. A consumer is not necessarily greatly influenced as to whether a side of leather is heavy weighing or light weighing if it cuts to advantage or within his cost limits and produces soles entirely satisfactory in the shoe. If the leather cuts too high, the manufacturer would not purchase it if he could avoid it beforehand. If it did not finish well and unusual complications arose when put in the shoes, it would be useless to him. But if the tanner were so successful as to produce sole leather that was adulterated or overweighted, but that did not give the shoe manufacturer any trouble or cut to a loss, he would undoubtedly continue to sell his leather and do business.

The one product that comes out of sole leather that has the highest value is the outer sole. The manufacturer wants to get first the greatest number of outer soles that he can out of his side of sole leather. You are doubtless aware that the part of the hide lying over the bony structure of the animal produces the firmest or best soles. The farther down into the skirts or shoulders that the production of suitable outer soles can be carried, and which are parts usually too soft and coarse for outer soles, the better the leather cuts. If the filling or loading of sole leather enables the cutter to get outer soles down into the skirts and into the shoulders farther than he would if the leather were not so filled or weighted, then he can afford to have the leather cost him more. As an illustration of this, take a side of leather that has not been over weighted but that weighs, ready for the

manufacturer to use, fifteen pounds and costs 30 cents per lb. We will assume that he gets thirteen pairs of outer soles out of this side, and a varying quantity of all the other less valuable products, taps, insoles, heeling, etc., that come out of the shoulders, skirts, etc., and on which he can and does value cost at once at prices that amount to 86 cents. Then the balance of the cost of the 15-lb. side, $3.64, must be placed on the thirteen pairs of outer soles, showing that from an ordinary Oak Back at 30 cts. per lb., they would cost or be worth 28 cts. per pair. Suppose he is able to cut fourteen pairs of outer soles instead of thirteen. He gains another 28 cts. or almost increases the value of this fifteen lbs. of leather 2 cents per lb.; so that the principal features for the consumer of sole leather to note is whether or not the side of leather he is contemplating will produce a maximum amount of outer soles. Now the moment the tanner forces extra or unusual weight into the side of leather without making it possible for the manufacturer to obtain an equivalent value or gain in outer soles, he lowers the value of the side of leather to the manufacturer and he must buy it cheaper. On the other hand, if the tanner should force into this 15-lb. side an extra pound of weight and also produce extra cutting qualities so that the manufacturer should get fourteen pairs of soles instead of thirteen pairs, it would make the side of leather almost 2 cents per pound more valuable and he would not care if it were weighted if it would finish and wear well.

As a matter of fact, the greatest difficulty, as we have attempted to show, has been with the materials cut from the shoulders and skirts or coarser, more open fibred part of the leather, probably due to the fact that this part of the leather absorbs more of the adulterating or weighting materials than the closer fibred parts of the leather and it comes to the surface and shows oftentimes in a white bloom or deposit or a dark, streaky look as though the leather had been oiled. It will be found to taste sweet, indicating in the eyes of the layman that the leather has been adulterated with glucose or some kindred material not tanning, and the bloom or white deposit will have a salty or acid taste which is generally said to be Epsom Salts

or something of that nature not tannin. When it is very apparent, the manufacturer at once is suspicious and refuses to buy the leather.

Experience with the different kinds of sole leathers in their daily use in shoes seems to be broadly this; that the manufacturer does not trouble himself about what is in the leather until it gets him into trouble and is unprofitable; and undoubtedly in the use of sole leather there is a point where weighting the leather does not become apparent or a difficulty to the manufacturer. Such a method of weighting it would seem was bound to be followed and used so long as it means extra profits to the tanner, and the shoe manufacturer can buy the kinds of leather that he must have within his range of cost prices; for the shoe manufacturer has to produce within very restricted lines of cost from a varying material which is practically out of his control. The selling prices of the different grades of shoes are practically fixed, sharply defined, well understood, popular retail prices prevailing from year to year. This puts the manufacturer in a position where he can only stand a certain amount of variation in the market or fixed cost of his materials as his whole shoe must come within a certain figure If his upper leather costs too much, he must balance it up somewhere in the shoe, or if the sole leather costs too much, he must, vice versa, take it out of the upper leather. Therefore, he has a certain basic price for the different sole leather parts and must produce them somehow from season to season, taking care of the varying market conditions and values partially by rearranging the different values in his shoes or by lessening the cost of his shoe by using cheaper classes of materials, a very difficult and dangerous thing to do.

There are so many conditions that have a bearing on the cost of materials entering into the shoes that it would be difficult to explain them all here in detail. But from this it can be seen that the tanner can easily compromise the selling value of his leather if he is tempted by abnormal prospective profits into weighting or adulterating his leather too much. Of course the tanner, like every other producer of a manufactured article, is going to use every possible means to cheapen

the cost of his product and increase his returns. He is going to adopt any new methods invented from time to time that redound to his benefit and, for this reason, is it likely that such methods will not be used? There is one possible way to stop it, and that is to sell sole leather by the foot or measurement instead of by the pound. This, however, would be revolutionary in its effect and entail the entire change of the system of cost accounting in present leather and factory methods and it is doubtful if it would be possible or practical to put such a method into general use.

Chrome tanned sole leather is sold by the foot. The undoubted reason for this being that the leather cannot be or is not weighted but is simply the pure hide fibre shrunk from its original spread and preserved by the Chrome process, and the tanner is not able to sell as many pounds weight to the square foot as he does in a weighted or bark tannage. Therefore, instead of selling such leather within the ordinary range of sole leather prices by the pound, that leather buyers are familiar with, for instance, 30 cents per pound, the tanner would have to charge 60 cents or 70 cents per pound, and the shoe manufacturer would be immediately badly prejudiced against it because of such an unusual price. Offering it by measurement, he has found that he can sell it at about the same price per square foot as he would ask for ordinary sole leather by the pound, a reasonably priced figure as viewed by the shoe manufacturer and, although the results are the same to the buyer in the cost of the sole, that is, it is very expensive leather to cut, he is better satisfied to buy it by the foot. This kind of leather is so small a part of the sole leather in use that it does not have any particular influence in the sole leather field.

As to the wear of the different kinds of sole leather as a whole produced to-day, weight for weight of sole, it wears fully as well or better than in years gone by, barring the softening proposition. The sole leathers analyzed and shown to have some foreign substances in them, have worn as well and have given as much satisfaction to the wearer of the shoes as shoes did when made in earlier years by old-fashioned methods. The adulteration of sole leather has injected new problems of

cost, etc., during the process of manufacturing and producing the shoe rather than in actual wearing qualities to the consumer. By this I do not mean to minimize the serious and prohibitive results to the consumer that take place when the leather is so loaded and stuffed that his counters and box toes will collapse or his shoes will, after wearing and absorbing some of the heat and perspiration of the foot, get into a chronic state of sogginess. Such a condition could not be endured and undoubtedly leathers that produce such results would be rejected at any price no matter whether the leathers showed a profit to the manufacturer or not, as he would not be able to make his goods stick with the buyer; but if a reasonable amount of weighting means more outer soles to be produced out of a side of leather and that give as much wear as leather ever did and perhaps more, that the shoe manufacturer can finish, and which will give as much wear as the so-called old-fashioned, bark tanned leathers have given in past years, then all things being equal, the tanner would be able to continue to produce his leather in his own way and not get into trouble, always and at all times understanding that the shoe manufacturer expects to and must cut his leather at a gain.

Referring to the use of English sole leather for which the English consumer has a very deep and favorable prejudice, there seem to be at least two distinct kinds of so-called Oak leather produced in England; one, the best leather made in very small quantity, taking about a year to tan, but guaranteed to be nothing but pure hide fibre, thoroughly tanned but not loaded with any foreign substances. The other line of leather which is even better in color, more solid in feel, plumper in weight, and apparently carrying more wearing qualities, is admitted to be tanned by a wholly different process, to be very heavily weighted, and sells in the open market for much less cost per pound, is used year in and year out with success by the English manufacturer, for all his shoe purposes and apparently for any purpose where great wear and strength is the dominating feature. There may be some leathers produced in this country as highly developed from an adulterated standpoint as the English leather, but if so, this has not become apparent.

Within a comparatively few years there was a deep prejudice among the manufacturers against the so-called extract tanned leather, due to undeveloped methods of tanning and to their not being acquainted with the product. Leather so produced could not be manipulated by the common methods with which the manufacturer was familiar in his processes, and, when the leather first came on the market, it met with a slow acceptance. It seems to have been of necessity and inevitable method of tanning and creates very little comment or distinction among the manufacturers to-day if the leather works right in the shoes.

In the Oak and Union field, experience shows that the leather produced in this way resists water better, is fully as tough in fibre, and wears as long or longer than the ordinary so-called old-fashioned, loose, open fibred, bark tanned leathers. This class of leather has a reputation of being very heavy weighing leather, and it is the natural conclusion of the shoe manufacturer, because the leather has not produced for him a maximum thickness of sole to the minimum amount of weight per square foot. Such matters, however regulate themselves in time as every kind of leather seems in the long run to find a place where it can be used.

Almost any feature in the production or consumption of leather is capable of a wide difference of opinion and many points that you would like to hear about the most may not have been touched on. These it would be a pleasure to hear brought out in a general discussion of your members present.

THE TANNAGE OF SOLE LEATHER WITH MIMOSA BARK.[1]

By Hugh Garner Bennett.

The advances in the knowledge of tanning which have been made in the last decade, have indicated what is the most appropriate use of the many of the chief vegetable tanning materials, and laboratory experiments have shown what are the most economical methods for their employment. Indeed, it may now be safely said that the knowledge of the effect of the commoner vegetable tanning materials on the colour, weight, and general

[1] From the *Journal Society Chemical Industry*.

quality of sole leather made from them, is one of the greatest advantages of the British sole leather tanner over his foreign competitor. That further knowledge is desired on these questions has often been evident to the writer, by the receipt of inquiries as to the nature of the leathers produced by certain vegetable tanning materials if used alone, it being rightly thought that this knowledge will give the best guidance as to the most suitable manner of blending with other materials. The experiments here recorded were carried out by the use of mimosa bark alone, and it is hoped that the results given may be of use in this way.

It is now well recognized that the golden rule for all vegetable tannages is to start the tannage in weak infusions and afterwards to move the goods through liquors whose strength in tannin is gradually increased. The rate of increase in tanning strength must, in all cases, be sufficient to maintain an appreciable rate of penetration, for in sole leather tanning, the use of mechanical means for assisting penetration is not allowable. If, however, the rate of increase in the strength of the liquors is too great, harsh or drawn grain results, and hence it is exceedingly important to know the extent to which it is possible to quicken the penetration by rapidly increasing the strength of the liquors, without producing drawn grain. This differs for every vegetable tanning material. With the so-called "astringent" tannins (*e.g.*, quebracho), the rate of increase in the strength of the liquors must be slow, and the infusions used in the early stages of comparatively small strength, whereas with the so-called "mellow" tannins (*e.g.*, gambier), distinctly stronger infusions may be used, of which the rate of increase in strength may also be greater. Hence in the ordinary mixed tannage of sole leather, the mellow tannins are employed in the early stages and the more astringent tannins in the later stages, which method is accomplished in practice by the system of working the liquors "down the yard."

As the tannin of mimosa bark is known to belong to the class of astringent tannins, it was thought worth while to carry out some experiments on a small scale, with the object of finding some method by which the tannins might be artificially "mellowed," so that stronger infusions might be used with impunity and a quick penetration obtained. It has been pointed out by

Procter that the presence of neutral salts in tan liquors is one of the important factors in producing mellowness, and it is now well known that a preliminary mineral tannage materially assists the rate at which goods may be penetrated by the vegetable tannins, hence the experiments recorded below were made to investigate the effect of adding various mineral salts to tan liquor made entirely from mimosa bark. Small pieces of pelt from an ox-hide belly, measuring about 9 inches in length by 4 inches in width, were employed for this purpose, and were immersed in the tan liquors without any deliming other than a very short washing in water. These were tanned in porcelain pits of about 8 litres capacity, and in each pit the strength of the liquor was the same, and increased at the same rate. This was accomplished by pipetting into each pit, day by day, equal volumes of strong mimosa liquor. In each pit were placed 8 litres N/20 acetic acid, and in this was dissolved the salt whose influence was being investigated. The barkometer strengths of each were then taken and increased 3° by the addition of the strong stock solution. The acidity of these liquors was then determined by Procter's lime water method, and the tannage commenced by inserting the goods. The tannage lasted altogether about two months; one month in "suspenders," increasing the strength of the liquors 1° Bkr. per day up to about 30° Bkr., and one month in "handlers," increasing the strength of the liquors 3° Bkr. every few days until a final strength of about 60° Bkr. was obtained. The pieces were then lightly oiled with cod oil, dried out, and finished. One experiment was carried out without the addition of any salts for the sake of comparison.

Salt employed	Amount of salt in liquor. Per cent.	Strength in acetic acid	No. of cc. lime water required by 10 cc. liquor	Bkr. strength at start
—	--	*N*/20	11.4	4°
Sodium acetate.....	3	"	11.7	13°
Calcium acetate.....	3	"	9.9	20°
Magnesium sulphate ..	3	"	10.7	19°
Sodium sulphite	3	"	12.1	16½°
Sodium sulphite	½	"	11.2	6°
Potash alum.....	½	"	3.5	5½°
Chrome alum.....	½	"	12.2	6°
Sodium sulphite	½	*N*/10	21.4	5½°
Magnesium sulphate ..	½	"	22.2	6½°
Potash alum.....	½	"	5.7	5½°

In all cases, the presence of salts caused a very distinct increase in the rate at which the pelt was struck through, a few days sufficient for all pieces except in that pit where no salts had been added. In all cases, also, when salts were employed, the pelt, after being just struck through, was extremely soft, the tannage being obviously unsuitable for sole leather. Where no salt was employed, however, the result was much firmer, and quite promising for sole leather goods. Each of the salts had also its effect upon the color of the goods. The acetates of calcium and sodium gave a distinctly darker tinge than when no salt was used, and the chrome alum also gave a darker color on account of the chrome absorbed. By the use of magnesium sulphate, potash alum, and sodium sulphite, however, some improvement in color was obtained, especially in the case of the sulphite, which produced a much lighter colored result in the early stages, but which, on the other hand, also yielded by far the softer result. When less sulphite was employed the effect both in lightening the color and softening the goods was distinctly less. It was found, further, that the softness caused by the use of these salts could be partly eliminated by using handler liquors which contained none of the salt, but when this was done the color of the goods rapidly became the same. In order, therefore, that the effect in improving the color should be at a maximum, it is necessary that the salts should be in the liquors throughout the whole process. Another series of experiments was carried out in precisely the same way as described above, but with N/10 acetic acid instead of N/20, with the object of discovering whether the softness resulting from the use of sodium sulphite, etc., could be prevented by the use of more acid. In this series, 0.5 per cent. of sulphite, potash, alum, and magnesium sulphate were used (see table above), and it was found that, in spite of the great increase in acidity, the difficulty was only partially overcome. Furthermore, in all cases the difference in color became less as the tannage proceeded and in the finished goods was scarcely appreciable.

From these considerations, it is clear that the employment of these salts for improving the color of mimosa tannage is of little practical value, and that their employment for "mellowing"

the tannin, and assisting in a rapid tannage should also be marked by considerable caution on account of their liability to give a soft result. The use of a very small amount of sodium sulphite to mellow a fresh mimosa liquor, into which green goods are to be placed, is perhaps the only opportunity where it would be wise to utilize these salts in the case of a sole leather tannage.

The results of the determination of the acidity of these liquors before use is also somewhat instructive as showing the effect of these salts on results obtained by Procter's lime water method. As saturated lime water is slightly weaker than N/20, it was to be expected that rather more than 10 c.c. would be required to give a permanent turbidity with 10 c.c. of the liquor, and although this is usually the case, a curious anomaly occurs in the presence of potash alum, in which case a turbidity is obtained long before the acid present is neutralized. It has recently been shown (*Collegium*, 1908, 357) that tannin in the presence of sodium sulphate is an extremely sensitive reagent for the determination of aluminium salts, by the formation of a colloidal precipitate, and it may be that the turbidity here obtained is due to the precipitation of a similar compound.

The strong mimosa liquor used for strengthening the tanning liquors in the above experiments was obtained by leaching the mimosa bark in a battery of experimental leaches, consisting of six cylindrical copper vessels fitted together on the press leach system. The bark used was ordinary Natal bark, which, on analysis, gave the following results:—Tannin, 37.0 per cent.; soluble non-tannins, 9.5 per cent.; insoluble, 42.1 per cent.; water, 11.4 per cent. Each leach vessel was filled with bark, and hot water was poured on to the first of the series from time to time, to press the liquor forward into the other leaches, which were filled at the rate of one per day. When all were full, the barkometer strengths of the liquors in each were taken, and found to be as follows—

(1)	(2)	(3)	(4)	(5)	(6)
0°	2°	2°	7°	18°	50°

This shows how very rapidly the bark yields up its tannin to water, and hence permits the preparation of exceedingly strong

liquors by leaching only. It was found that by continuing to press round over fresh material, it was possible to obtain with comparative ease liquors varying between 130° and 170° Bkr., and liquors obtained in this way were employed in the experiments recorded above. This point is of obvious practical importance, both to manufacturers of mimosa bark extract and to tanners who employ any considerable proportion of the bark. In spite of the apparent ease with which the material "spends" in leaching, however, it is an extremely curious fact of considerable economical significance, that the apparently spent bark still contains appreciable quantities of tannin, which can only be leached out with some difficulty. This is well illustrated in the spent tan from the hot water leach (vessel (1)), in the experiment recorded above, which would appear to be completely exhausted when judged by the strengths of the three weakest liquors, but which, on analysis, yielded the following results:—

Analysis of spent tan.	Per cent.	Stated on original material.	Per cent.
Tannin	5.8		2.6
Soluble non-tannins	1.0		0.5
Insoluble	93.2		42.1
Water	0.0		11.4
		Leached out	43.4
	100.0		100.0

The author now carried out a practical investigation in the experimental tannery on the manufacture of sole leather by means of this same bark. As the liquors had to be made up as required from fresh leach liquor, it was necessary to commence the tannage with very weak infusions just as in the laboratory experiments, but some mellowness was imparted by the addition of one-half per cent. and one-eighth per cent. of sodium sulphite to the first and second suspenders respectively when they were first made up. There was nevertheless in each of the packs taken through a tendency to draw grain, especially in the offal, and contrary to what might be expected, the liquors did not seem to mellow in the slightest by passing goods through them. In an ordinary mixed tannage the astringent tannins

are in preference absorbed by the hides, and hence as goods pass through, the liquors become increasingly mellow; the fact that this does not happen with a pure mimosa tannage seems to indicate that mimosa bark contains only astringent tannins, and perhaps even only one chemical individual.

It also became evident that the pure mimosa liquors had little or no "souring" properties, *i. e.*, that the material had a very small capacity for producing organic acids by the fermentation of the sugary matters naturally associated with the bark. These acids swell the fibres and thus act in the opposite direction to the astringent tannins, so that it is important to have the correct ratio of acid to tan throughout the whole of the tanyard liquors. It was found that although the early liquors in the mimosa tannage were somewhat weak in tan, the great astringency of the mimosa tannin caused the necessity for an acidity appreciably greater than is now commonly found in the sole leather yards of this country, and as these acids were not developed in the liquors by natural fermentation, it was found necessary to add acid to the tan liquors throughout the whole process. A laboratory experiment showed that if acid be used to the requisite extent in the early stages and the goods be placed in stronger liquors which had not been artificially acidified, the leather soon became quite soft and flexible and quite unsuitable for sole purposes. Hence in the practical work acid was added to every tanning liquor. A good quality acetic acid was used for this purpose until the strength of the liquors in acid ranged from $N/23$ up to $N/10$ approximately. The necessity of this addition of acid is a serious disadvantage of the material and makes it quite out of the question to use mimosa bark alone when tanning on a large scale. It is probable that myrabolams would form an exceedingly good blend with mimosa, not only on account of its souring qualities, but also on account of its comparative mellowness and its beneficial effect on color.

The tannage given by the author to the goods in this case was with mimosa bark only, and lasted about three months. The process is specified in the following table:—

Nature of liquor	Time in each	Barkometer strength	No. of cc. lime water required by 10 cc. liquor
1st suspender.....	3 days	6°	10
2nd "	3 "	10°	11
3rd "	3 "	15°	12
1st handler.....	7 "	22°	13
2nd "	10 "	27°	14
3rd "	14 "	32°	15
1st layer	1 week	50°	16
2nd "	2 weeks	60°	20
3rd "	3 weeks	70°	22

On coming from the last layer the goods were drained overnight, scoured, oiled, sammed, pinned by hand, lightly rolled, dried further, heavily rolled, and dried out. They were finally brushed by machine.

The resulting leather was firm and of good quality, and considering the red color of the bark and of the liquors which are yielded from it, the color of the goods was remarkably light, being only slightly pink. This pink can be partly eliminated by bleaching with sulphurous acid, but soon returns if the goods are exposed to light. An analysis of the finished leather gave the following results:—Hide substance, 34.5 per cent.; tannin and organic matter, 51.2 per cent.; ash, 0.3 per cent.; moisture, 14.0 per cent. As would be expected from this analysis, the weights obtained were also good; one butt, for example, gave a pelt weight of 28 lb. and a leather weight of 20 lb., which is a yield of 71.4 per cent.

The thanks of the author are due to Prof. H. R. Procter for suggesting this investigation and for much helpful criticism and advice during its execution.

BOOK REVIEW.

The Design and Equipment of Small Chemical Laboratories. RICHARD K. MEADE, B.S. The Chemical Engineer Publishing Co., Chicago, 1908. 136 pages.—This book, part of which has appeared in articles for the *Chemical Engineer*, is intended for the guidance of the young chemist in equipping a practical laboratory for the works, and seems well fitted for that purpose. The work is plentifully illustrated with outline drawings and some dealers' wood-cuts.

The first chapters are devoted to general arrangements with sketch floor plans, etc. The good principle of a separate place for different operations

is emphasized and details given for the relative positions of sinks, work-tables, hoods, etc.

With regard to the broad subject of apparatus, the book is comprehensive and little seems to be omitted. Being condensed, the treatment is essentially a list or classified catalogue of select approved forms found in the market.

The chapters on burette work, weighing and heating appliances are detailed considerably. Special chapters on such specialties as assaying and electro chemical analysis are included.

ABSTRACTS.

A New Method of Testing Leather. W. FAHRION. *Chem.-Ztg.*, 1908, No. 75, reprint *Collegium*, 1908, Nos. 338-39, pp. 495-501.—When natural hide is dried, its original water content of 80 per cent. is reduced to 15 per cent., and it becomes hard and transparent. The softness and pliability which characterizes natural skin is due to the separation of the fibres by water, and on drying these adhere together. The object of tanning is to overcome this; Knapp defines leather as animal hide in which by some means the fibres have been prevented from sticking together on drying. The water of hide may be extracted by alcohol, and on drying the hide again takes up 15 per cent. of hygroscopic moisture, retaining air in its pores and remaining opaque. It is, however, restored by soaking to the condition of the original hide, and is therefore no genuine leather. The modified definition of leather is: animal hide which after treatment with water remains flexible and soft on drying.

Laboratory experiments in tanning are best made upon skins from the tannery which have been through the operations of softening, liming and dehairing, including plumping and bating. For preservation, these may be dried and when required, treated with water till 80 per cent. is absorbed. The soft hide may also be preserved in water containing one-half per cent. sublimate. Besides water, alcohol and other solvents may be used for applying the tanning materials; it is first necessary to expel the water in the hide by the solvent in question.

To determine experimentally to what extent leather has been formed, the above definition cannot be applied practically, especially with hide powder which is especially suited for this work. The behavior of the product with boiling water is made use of. By such treatment, raw hide is converted entirely into glue, chamois leather but slightly so, vegetable-tanned leather gives glue tannate, and chrome leather is unaffected. The resistance of leather then to boiling water gives a measure for the degree of tannage. The author's hot water test is carried out as follows: 1 grm. of the finely divided material is heated in a 100 cc. standard flask of Jena glass with 70 to 80 cc. distilled water for 10 hours in boiling water, shaking occasionally and replacing the water evaporated. The solution cooled to 75° is then made up to the mark, filtered through linen. Fifty cc. of the filtrate are evaporated, dried at 115° to 120° to constant weight. The residue is ignited, again weighed and the difference $\times$ 200 = per cent. solubles. In a second sample

of the original material, the moisture and ash are determined. The content of insoluble organic material expressed in percentage of the original substance, water and ash free, is rated as water proof, and is the measure for leather formation referred to. The method gives results concordant enough for comparisons, and has given the author good service.

Material	Water	Ash	Soluble	Water-proof
Hide powder (a).....	17.0–13.0	0.2	78.1–82.8	0.0–5.7
Hide powder (b).....	14.2	0.4	82.4	0.5
Chamois leather.....	19.7	5.6	14.6	80.5
Vegetable tanned:				
Sole leather.....	13.1	1.3	39.8	54.5
Upper leather.....	16.2	0.5	25.0	70.0
Chrome tanned:				
Weak chrom'd hide powder	13.3	1.3	59.0	30.9
One bath leather.....	15.9	5.8	8.5	90.4
Two bath leather.....	18.3	6.6	10.2	86.4
Wool.....	9.3	1.6	1.2	98.7

The view is sometimes advanced that hide contains albuminous substances which are important in tanning. If this were so, they would be coagulated in the hot water test instead of going entirely into solution. It is more probable that hide is either a chemical individual or a mixture of very similar substances, as concluded by von Schröder and Paessler, in the former's "Gerbereichemie." The high ash in chamois leather is due to the liming and is variable. The soluble found in this leather was pure glue, which could be precipitated by tannin. After the hot water treatment, the insoluble was no longer leather, but after drying, an elastic, friable mass. In the case of the vegetable-tanned leathers, the tannin was in excess and separated out on cooling, amounting to 16 per cent. difference in solubles with sole leather. The insoluble glue tannate formed is half liquid while hot and hardens on cooling; it is soluble in alcoholic alkali and the solution freed from alcohol and acidified, precipitates part of the tannin, as is the case with a direct extract from leather with alcoholic alkali. An ideal leather of 100 per cent. water-proof is not attainable nor practically desirable, but the hot water test may be used in judging regular products.

Breinl (*Ztsch. angew. Chem.*, 1888, p. 690) has found that wool goes completely into solution with water in a sealed tube at 150°; here it is scarcely attacked. May not wool differ only from sheep-skin in being after a fashion tanned? The ultimate analysis for C, H and N is much the same, and experiment shows that wool contains a small amount of fatty derivatives insoluble in ether, and may be held to be analogous to chamois leather.

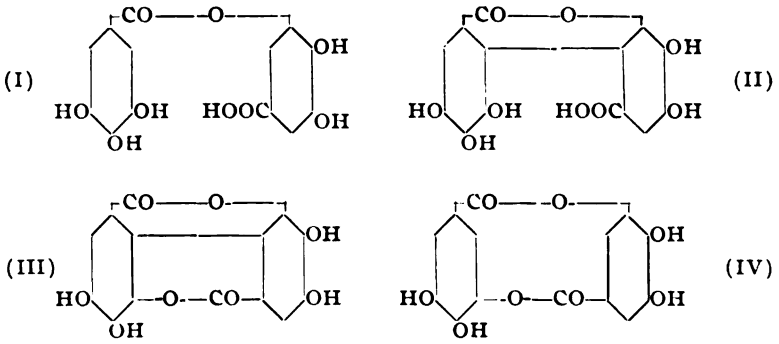
Compounds of Gelatine and Tannin. J. T. Wood, *Collegium*, 1908, No. 338, p. 494.—At the time the author published his paper on tannin precipitation by gelatine (JOURNAL, 1908 [3], p. 183,) he assumed the compound to be of constant chemical composition. Following since suggestions made by Dr. Stiasny and Prof. Procter, he has found that the amount of tannin precipitated is greatly reduced by depriving the gelatine of its mineral matter. It has also been found by Weiske that addition of an electrolyte

brings about an instant precipitation. The conclusion is that the precipitation is a colloidal one, complicated and variable with the conditions. As the situation is very similar in tannin analysis, it is remarkable that results are concordant as they are. The colloidal nature of the reagents require strict adherence to every detail of the analysis.

Valuation of Willow-Bark according to von Schroeder's Hydrometer Method. APPELIUS AND MERKEL. *Gerber Zeitung*, 1908 [51], No. 296.—Willow-bark is an excellent tanning material and although little used in Germany because of scarcity, is much employed in Russia. Willow-bark from Russia was used in these investigations, 100 grms. being extracted 24 hours with 1 litre water at 15° C. A comparative table is given of specific gravities of solutions from 0.48 to 1.0° B., with corresponding percentages in tans. Check analyses showed a fair agreement and the method is considered sufficiently accurate for valuing the bark commercially.

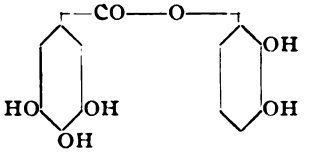
New Practical Method for Determining Tannin. L. E. CAVAZZA. *Chem.-Zentralbl.*, 1908 [2], No. 26, p. 2045.—The tannin is precipitated by lime water in a funnel, the tube of which is closed at the bottom. The height of the precipitate after settling is read off the tube which has been previously calibrated with precipitates from known amounts of tannin, 1, 2, 5, 10 mgs. One cc. of calcium tannate here corresponds to less than .00003 grms. tannin.

Constitution of Tannin. M. NIERENSTEIN. *Collegium*, 1908, No. 339, pp. 502-4. The author has already shown that on oxidation of tannin in acetic acid solution by potassium persulphate in presence of concentrated H_2SO_4, ellagic acid is formed; this favors the assumption of digallic acid as a component of the tannin complex. By the use of hydrogen peroxide as the oxidizing agent, the author has succeeded in oxidizing tannin (I) in part to ellagic acid (III), also obtaining the intermediate product (II), which he terms luteoic acid (Luteosäure)



Thirty grms commercial tannin were boiled with 20 cc. peroxide and one-half litre water for 2 hours (inverted condenser), the solution becoming red and separating 8 grms. of a red powder analyzing for ellagic acid. The

mother liquor concentrated one-half separated reddish brown crystals of luteoic acid $C_{14}H_8O_9$. It differs from ellagic acid in being soluble in alkali with a red brown color; it dissolves in concentrated H_2SO_4 with formation of ellagic acid. It decomposes with gas evolution at 338 to 342°. On warming with 10 per cent. soda solution, it changes to ellagic acid. Acetylized, it gives tetra-acetylellagic acid. The ordinary methods for eliminating the carboxyl group failed, but by treatment with hydriodic acid (Fittig and Binder's method with cinnamic acid), after 5 days exposure to daylight there was a complete separation of pentaoxybiphenylmethylolid,

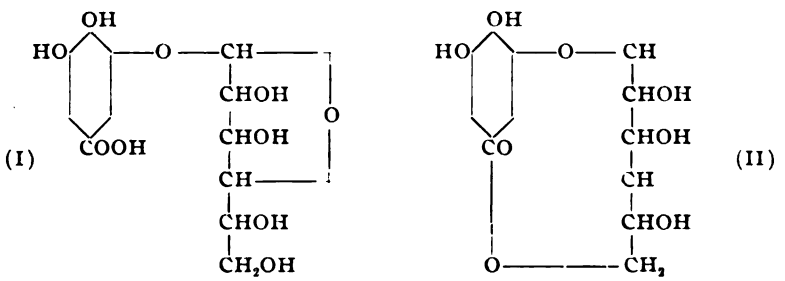


This forms yellow leaflets, crystallized from alcohol, melting point 259 to 262°.

Tetra-acetyldigallid (IV) was prepared from acetyltannin dissolved in pyridin and slowly mixed with pyridin containing phosgene. The product separating was boiled with acetic anhydride, precipitated with and recrystallized. The formula confirmed by analysis and acetyl determination is $C_{14}H_4O_8(C_2H_3O)_4$; melting point 130 to 132°.

Acetyldigallid oxidized with hydrogen peroxide gave ellagic acid. Hydrolyzed by boiling with dilute H_2SO_4, it gave gallic acid.

Tannin Constitution. K. FEIST. *Chem.-Zeitung*, 1908 [32], pp. 918-19.—Since tannin is dissociated by water, the author has prepared the material for his investigations with exclusion of water, extracting the gall-nuts with chloroform, benzene and ether. By fractional extraction with ether, a small amount of a yellowish substance was obtained, melting at 233° with decomposition and resembling tannin; it differed from it in giving no precipitate with albumen or quinine salts. Molecular weight (boiling-point method), 317. On hydrolysis, gallic acid and glucose were obtained. The substance was named glucogallic acid, and is assumed to be an ethereal compound of gallic acid and glucose, either $C_{13}H_{16}O_{10}$, the acid form (I), or $C_{13}H_{14}O_9$, the lactone form (II); the analysis agrees better with the last.



The tannin extracted with acetone could only be obtained amorphous and

according to capillary analysis was a single substance; molecular weight 615. The rotary power was greater than that of commercial tannin. It yielded glucose, which is doubtless the cause of the optical activity of tannin and glycogallic acid. On hydrolysis, the greater part of the gallic acid was easily separated, but a small amount separated with difficulty as with glycogallic acid, showing that gallic acid is united with glucose in different ways. The constitution given to gall-nut tannin is that of an ethereal compound of glycogallic acid with two molecules of gallic acid of the lactone form, $C_{27}H_{22}O_{17}$, mol. weight 618.2, or the acid form, $C_{27}H_{24}O_{18}$, mol. weight 636.2.

Additional Remarks on the Extraction of Tanning Materials. W. EITNER. *Der Gerber*, 1908 [34], Nos. 820-23, pp. 291, 305, 319, 333.—This is supplementary to the author's paper on rational tannin extraction of last year. He first points out the importance of keeping in mind the use which is to be made of the extracts obtained. The usual practice is to extract the maximum amount of tans possible, and many tanners strive for results based upon the chemical analysis. It must be considered, however, whether the different tan-stuffs possess equal tanning power or tan in the same manner. Only those tans are available which remain in solution at the temperature of the tanning operation. This temperature, may be increased, however, as the tanning advances, since hide resists heat better the more it is tanned. The analytical control of the extracted material is correct only for a few simple materials like sumac or gall-nuts, which contain but a single tan-stuff. Most materials are complex and yield at high temperatures difficultly soluble tans which deposit a sediment on cooling. The author has examined a large amount of technically extracted material and finds that in general practice, tanning material is well utilized, and that less useful substance is thrown away in waste bark than many think. This is due principally to the ready solubility of the really useful tans. The ratio between useful and useless tans in material will vary not only according to the kind of material, but also in the same material according as it is fresh, or already partly extracted. From the material employed for dusting layaways, only the easily soluble tans are removed. The used material will then contain relatively large amounts of difficult soluble tans which can only be extracted at high temperatures. The solubility of these is also lowered by the presence of acids which have been formed during standing in the vats. The liquors obtained by extracting used material are best suited for fore-tanning and plumping, and are also used with advantage in extract tannage in the handlers. On extraction at 60°, a liquor is obtained which contains only soluble tans without sediment, and also retains the acid. If the material be extracted boiling, however, acetic acid is lost and the less soluble tans go into solution, but deposit on cooling. The analysis of the spent material shows better, but there is no real advantage. Fresh and used material should be extracted separately.

Some analyses are next quoted. Slovak pine bark, 13.5 per cent. tans after leaching for fore-tannage of sole leather, gave 2.62 per cent. tans; the extraction was carried out boiling in the last three vessels of a battery of 8.

Nevertheless the proprietor was not satisfied with the effect. An experimental extraction in the same battery without boiling, adding hot water to the last vessel, gave a spent bark of 5.8 per cent., which proved to be entirely difficult soluble tans. A Carinthian pine bark, leached in a battery of 7, gave 4.06 per cent. residual tans, all difficult soluble. A Styrian pine-bark (12 per cent. tans), extracted in a series of 8 with steam, yielded a residual bark of 4.39 per cent., all difficult soluble. The leaching in these four examples is considered sufficient, the second being the most rational, although leaving most residue. Another Syrian bark (old), after leaching, gave even 6.8 per cent. tans, all difficult soluble. Similar results were obtained with used pine bark from layaways, containing 9 per cent. tans; on extraction in a battery of six vessels, boiling out with steam in the last, a spent bark of 5.5 per cent. tans, all difficult soluble, was left. This material came from the same tannery as No. 3 above, probably the same original bark. The different result obtained in this last extraction is attributed to the acid in the bark from the layaways. Some samples of leached pine bark showed 7 to 8 per cent. tans, part of which was still useful; these could not be determined directly, but the useless tans were found to average 5.5 per cent. From all the above it is probable that leached pine bark of about 5 per cent. tans (lower with young bark, higher with old), contains nothing useful; this amount should be deducted from the analytical returns in computing costs.

With oak, the spent bark from six tanneries ranged from 1.7 to 2.7 per cent. tans.

Quebracho wood is always extracted hot; its difficult extraction is not due to the hardness of the wood, but to the peculiar nature of its tans. Of the 20 per cent. total, 10 per cent. are easily soluble, 8 per cent. first above 40°, and 2 per cent. (resinous) at boiling. As an average from several tanneries, 3.5 per cent. tans were found in the residue from extraction in open vessels, and 1.8 per cent. when extraction was carried out under pressure. In both extractions the useful tans are exhausted together with some which are useless and even injurious in tanning. The extract makers, by the use of chemicals, make this last available.

Myrabolams are frequently extracted in tanneries. Analyses of residual materials from extraction under pressure gave 2.8 to 3.7 per cent. tans; these were less colored and more soluble than the residual tans in spent bark and wood, but they separate at the temperature of tanning and are ineffective. Residues from open extraction of ground material contained 6.7 to 8.2 per cent. tans; 7.5 per cent. probably represents then good utilization.

Samples of spent mallet bark from four different places gave 9.4 to 9.8 per cent. tans.

The other tanning materials in use are seldom extracted singly. Data are available for galls and valonia, which have already been used for layers. The dried material from the layers contain 18 to 26 per cent. tans according to their position, and after extraction, 12 to 18 per cent are utilized. Metallic or cement vessels should not be used for extracting sour material, but rather vessels of wood.

Results are also given for residual tans from various extractions of mixed materials. It was found that these agreed on the whole with the computed results from the data for extraction separately.

In conclusion, since the useful tans can be readily obtained with the ordinary extraction apparatus, it is doubtful if there is any gain in using the various new forms claiming increased effect.

School of the Tanner (continued); **De-liming.** A. SCHMIDT. *Le Cuir*, 1908 (1), No. 15, pp. 5-7.—If lime be left in the hide, it rapidly injures it; the air converts the lime into carbonate, which in large hides fills the pores, preventing absorption of the more useful tannin. A gain in weight by such means has little to recommend it, which applies also to the neutralization with sulphuric acid, giving likewise an insoluble salt. Moreover, the presence of lime causes spots and an irregular color of the leather, and when this is to be blacked the color takes irregularly without remedy. When ready for tanning, the skin should consist only of pure hide and water. The sole method is to convert the alkaline lime with some acid into a soluble lime salt to be removed by washing. This is the only operation in leather making which can be followed and controlled by chemical test. A small cutting of the thickest part of the hide is soaked in water containing a little phenolphthalein; this should not be reddened when the lime is completely removed. Hides spotted on the grain with red, violet or gray, to be seen in many tanneries, show incomplete de-liming which might have easily been avoided by using the above test. It should be added that a careful, complete de-liming does not make any less necessary the following mechanical operations, especially those upon the grain. There must still be removed the refuse formed from the fat of the skin, either by hand or by machinery; if not thoroughly done, the tannage is irregular. After this preparation, the hide will be considerably shrunken, but its volume will be restored by the subsequent swelling in the initial tannage or in a special plumping bath. The various means used in de-liming will be described in the next article.

Discussion Relating to Large Liming and Tanning Vats (continued). *Gerber Zeitung*, 1908 [51], No. 300. *No. 245, continued.*—Drum tanning, while much used, is an incomplete process. The butts are too strongly limed, and as a rule, chemicals are introduced so that the leather may not need bleaching. If the extracts used are soluble enough to give light colored leather direct without chemicals, the leather is rarely good. Whenever the object has been to get fine colors, either by bleaching, use of cold soluble extracts, or adding chemicals during drum tanning, the leather has suffered. The sediment from commercial extracts is a hindrance to rational tanning as well as the great quantity of uncombined tans in the hide. This can be avoided by using tannery made extracts.

Precautions in Storing of Leather. *Gerber Zeitung*, 1908 [51], No. 297.—The best leather may deteriorate if not properly stored. The mould fungus requires for its development moisture and heat, and these prevail in spring at the beginning of the hot season. During the cold and moist season, the

leather absorbs water, the content being greatest in November to March and then gradually falling off, reaching minimum in July. The moisture of the leather disappears most rapidly in contact with dry air, and to prevent mould formation a continual and systematic airing of the store-room is necessary. The windows should however be closed during rainy or damp days, and generally at night. The leather should also be frequently shifted in the stack. Any mould appearing is wiped off the individual hides with a rag, outside the store-room in a well aired place. If in spite of these precautions, a vigorous growth of mould appears, then each hide must be wiped off and eventually the stock room thoroughly disinfected. The hides are carried out, a small coke furnace brought in and kindled, and after the room is well warmed, a few handfuls of flowers of sulphur sprinkled on the coals and the whole left over night. The next day, the ceiling, walls, and floor are thoroughly swept.

In airing the leather, the drying should not be pushed too far, not only for financial reasons (loss of weight), but also to avoid making the leather brittle. Over-dried leather may also take up so much moisture during working as to become spongy.

Salt Stains in Hides. *Le Cuir*, 1908 [1], No. 15, p .21.—The French syndicate of dealers in crude hides offer a prize of 2000 francs for the explanation of and remedy for saline pits and spots in hides.

PATENTS.

Process for Stretching and Straightening Leather Belting. U. S. Patent No. 908,957. M. H. AND C. G. COOK, San Francisco, Cal.

Apparatus for Stretching and Straightening Leather Belting. U. S. Patent No. 908,958. M. H. AND C. G. COOK, San Francisco, Cal.

Evaporator. U. S. Patent No. 909,028. C. L. SCHALITZ, San Francisco, Cal.

Leather Stretcher. U. S. Patent No. 909,123. F. J. RUPPEL, Baltimore, Md.

Leather Splitting Machine. U. S. Patent No. 909,157. A. A. CHILSON, Salem, Mass.

Process for Enameling Leather. U. S. Patent No. 909,288. B. B. GOLDSMITH, New York.—The process of enameling leather which consists in supplying it with a surface containing pyroxylin and then applying thereto a solution containing pyroxylin and boiled linseed oil.

Manufacture of Tanning Extracts. U. S. Patent No. 909,343. D. STEWART, Inverness, Scotland.—The process of manufacturing tanning extracts and liquors, which consists in passing successively through vats or pits containing tannin-containing material waste sulphite liquor whose ash contains not more than 6 per cent. of iron calculated as FeO, and then settling out difficultly soluble substances and concentrating the clear liquor.

Leather Working Machine. French Patent No. 393,019. F. J. PERKINS AND J. W. SMITH.

Depilating and Leather Working Machine. French Patent No. 393,453. A. G. MOENUS.

Process for Strengthening Leather. French Patent No. 390,122. M. BRIHAYE.—A dressing containing a base of gelatine is applied to locally strengthen the leather used in shoe manufacture, etc., enabling the usual reenforcement with paper, leather, etc., to be dispensed with.

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EDITORIAL.

The Conventions of our Association should be held every two years instead of annually, as at present. This change would certainly increase the attendance, and would not lessen the interest in our work; and it would also decrease the possibility of hasty conclusions drawn from hurried experimental work. A year is too short a time in which to report more than progress in some of the subjects under committee investigation. These investigations frequently develop conditions, that make other experiments desirable before a report is tendered; with the short time at the disposition of the committee chairmen, and knowing of the routine demands on the time of the members of the committee, the chairmen are tempted to present their reports, and suggest the desirability of getting results from the secondary experiments, before accepting the conclusions as final. With two years in which to complete the assigned work, it would seem that in any but the more complex subjects, a confident finality could be indulged in by the chairmen.

With the annual meetings the members will not make the effort to attend, that they would in the case of biennial gatherings. Our country is large, and the time and money consumed in traveling to an annual meeting is sufficient to become a matter for consideration on the part of most of us. With biennial meetings, at least half of this non-attendance cause is removed, and the other half will be readily absorbed by the simple fact that the meetings *are* biennial.

If the conventions are held every second year, they could be called for the year between the Conference years of the I. A. L. T. C., in which case each association would have an opportunity of testing and criticising the conclusions of the other. If the meeting years of the two associations were coincident, both bodies could pursue the same lines of investigation during the interim, and this would certainly lead to a closer union.

The term of office in our Association has lately been increased to two years, and it seems logical that committee terms should be made the same, and this would naturally mean biennial conventions.

Another change that should be made in the administration of

this Association, relates to the method of electing officers. Nominations are now made by mail and the nominees thus selected are voted for at the convention. Regardless as to whether the present method of determining the nominees is continued, the method of electing should be such as to allow every active member the privilege of registering his choice. It is hardly in keeping with the elaborate arrangements for nominations, to allow the final choice to devolve upon the members present at the convention. If the entire active membership is to participate in the nominations, the entire active membership should participate in the final choice. If it is not deemed wise to attempt the two mail votes that this would require, then constitute the Council a nominating committee, and let the entire active membership vote on the nominees.

We are in receipt of the first issue of *Leather*, an English monthly under the editorial guidance of Mr. M. C. Lamb, the well-known authority on the dyeing and finishing of leather This new publication intends to deal with the technical and practical side of the industry, and if it can fill the recognized demand for such an English periodical, it must succeed. With the continued support of the class of writers represented in the initial number, it should fill the demand, and if for no other reason than that of national pride, *Leather* should have the support of the many English leather chemists competent to contribute technical and practical articles.

Space reservations for proceedings of trade organizations are provided for, and this evidence of acumen should bring its tangible reward. We question the utility of a price list of tanning materials in a publication of this kind; it cannot be universally accurate, it could be misleading, and on the whole seems superfluous.

Mechanically, the magazine is pleasing, of a high order of workmanship, and entirely consistent with its indicated literary merit.

THE THEORY OF TANNING.

By Robert W. Griffith.

It has been asserted that in the art of tanning there is no relation between Theory and Practice. Those of the latter school claim that they alone are responsible for the progress which the industry has made and is making. The theorists on the other hand advance no claims as to what may or may not be accomplished as a result of their researches, but it cannot be denied that their efforts add materially to the common fund of knowledge.

Practice is wont to scoff at theory but the former should realize that the essential and fundamental principle of Theory is that it must be sound in practice. If theoretical principles are not sound in practice then they become hypothesis and not theory. The relation between Theory and Practice is then, the same as exists between Cause and Effect.

If then, for no other reason than that of mental recreation, practical men should consider the problems of their industry and contribute their share of knowledge to aid in the advancement of the industry. In building up the science of the tanning industry the contributions of practical and intelligent observation are as essential as the data contributed from the laboratory. The primary object of this paper is to review the most recently advanced theories of tanning from the standpoint of common practice. It does not aim at destructive criticism, but rather to be constructive.

Stiasny in his recent excellent paper,—"Critical and Experimental Contributions to the Theory of the Tanning Process," (This JOURNAL, 1908, p. 246), discusses at some length the theories previously put forward, analyzing them in detail, disputing many points and advancing experimental data in proof of his contentions.

Fahrion's theory that the tanning process is essentially an oxidizing one, comes in for a good deal of criticism. Stiasny proceeds to demonstrate by experiments that this theory cannot be substantiated, on the ground that hide fibre previously treated with a weak solution of peroxide of hydrogen, looses none of its

affinity for free acid or alkali. He further urges that the combination of hide substance with acids or alkalies from aqueous solutions is not to be explained by a chemical reaction. Stiasny describes many interesting experiments in proof of this and interprets the results obtained to support his own views. Stiasny next proceeds to discuss the chemical theory advanced by Nierenstein. This theory assumes a decomposition of the hide constituents brought about simultaneously with the decomposition of the tannin bodies and suggests a chemical combination between the two decomposition products resulting in the production of leather. It is difficult to reconcile this theory with practical observation and Stiasny's experiments do not support it. All of Stiasny's experiments are not, however, apparently as conclusive in demonstrating the erroneousness of the chemical theory, although his own conclusions are opposed to it.

In this critical spirit Stiasny treats with all the theories of tanning which can claim any serious consideration, and concludes that none of them fully explain what really takes place in the tanning process. Stiasny's own observations lead him to the conclusion that tanning is primarily an adsorption process and that the adsorbed substance undergoes secondary changes. This explanation involves an interesting discussion on colloidal and crystalloidal substances, but no light is thrown upon the nature of the secondary changes which the adsorbed substance admittedly undergoes. It is only in an explanation of these changes that a satisfactory solution of the problem is to be found.

Stiasny's experiments to disprove Fahrion's theory are by no means conclusive and whilst it may not be expedient to accept the latter's without question, yet it is not to be disregarded on the evidence which Stiasny brings against it. Stiasny's treatmen of hide fibre with peroxide of hydrogen, (HO.OH) does not prove that the fibre was oxidized by such treatment, and it is by no means clear why it should be. The essential feature in the theory of oxidization is the vehicle which conveys the oxygen atom. Now it does not appear that Hydrogen would suggest the most suitable vehicle. In the compound HO.OH, if we replace one atom of O with one of C, we have the compound H.COH, (Formaldehyde) and this substance is known

to have great affinity for hide fibre, and in subsequent experiments Stiasny shows that hide fibre previously treated with formaldehyde possesses less "combining value" with acids than when not so treated, a fact which supports the chemical theory, and would seem to indicate that the fundamental principle of tanning involves the employment of a suitable vehicle for Oxygen.

The one feature common to all tannages, both organic and inorganic, is the presence of the oxygen atom. Most investigators have directed their attention to the study of the tannages separately, and none have apparently looked for a principle common to all tannages. A consideration of the vegetable tannage in the light of recent investigations on tannin and gelatine compounds, (Wood) shows that tannin does not differ from the mineral tanning salts and the aldehydes in that it does not precipitate gelatine from solution under chemically pure conditions, but they all do render gelatine insoluble.

The question which now arises is whether it is the tannin or certain decomposition products of tannin which becomes responsible for the real preservative principle in the making of leather. The practical value of the bodies known as "non-tannins" is now recognized, and it has been demonstrated that an old tan liquor which showed no "tannin" by the hide powder analysis, was yet able to produce a good tannage on a skin treated with it. The "tannin" bodies are of such a nature that they readily break up into compounds of simpler constitution. Now it is reasonable to assume that tannic acid like all other organic acids, has a corresponding aldehyde, and it is probable that aldehydes are formed as the result of the breaking up of the tannin bodies in contact with the fibre.

If we may now assume that oxygen is the factor involved in the production of leather, a review of the conditions under which all tanning takes place tends to show that a colloidal condition of the oxygen vehicle is necessary for a complete tannage. This principle is well illustrated in the case of Chromic acid, CrO_3,—a crystalloid—which although easily taken up by the fibre, has no real affinity for it, but when this chromic acid becomes reduced to chromic oxide, Cr_2O_3,—a colloid—we have

a permanent tannage. In the case of the one bath chrome tannage, we have a process analogous to dialysis in which the base of the salt is retained by the fibre and the acid radicle liberated into the bath.

Experience has taught that the basicity of the chromium salt is the most important factor in the production of a satisfactory leather, or in other words, the completeness of the tannage depends upon the relation of the oxygen to the mineral base, and the closer the union is between these two bodies in their ultimate fixation upon the fibre depends the permanency of the tannage.

In investigating the theory of tanning from the standpoint of what is accepted in practice, it would appear logical to conclude that the transformation of hide fibre into leather depends upon the addition or subtraction of oxygen by means of certain vehicles, which enter into intimate contact with the fibre and bring about a chemical change in consequence, and this results in producing a product of higher molecular constitution than the original hide.

It is generally accepted that the primary changes in the tanning processes are brought about by physical agencies, but close observation and investigation point to the probability that the secondary changes are due entirely to chemical action.

A LABORATORY DRUM.

By W. S. Loud.

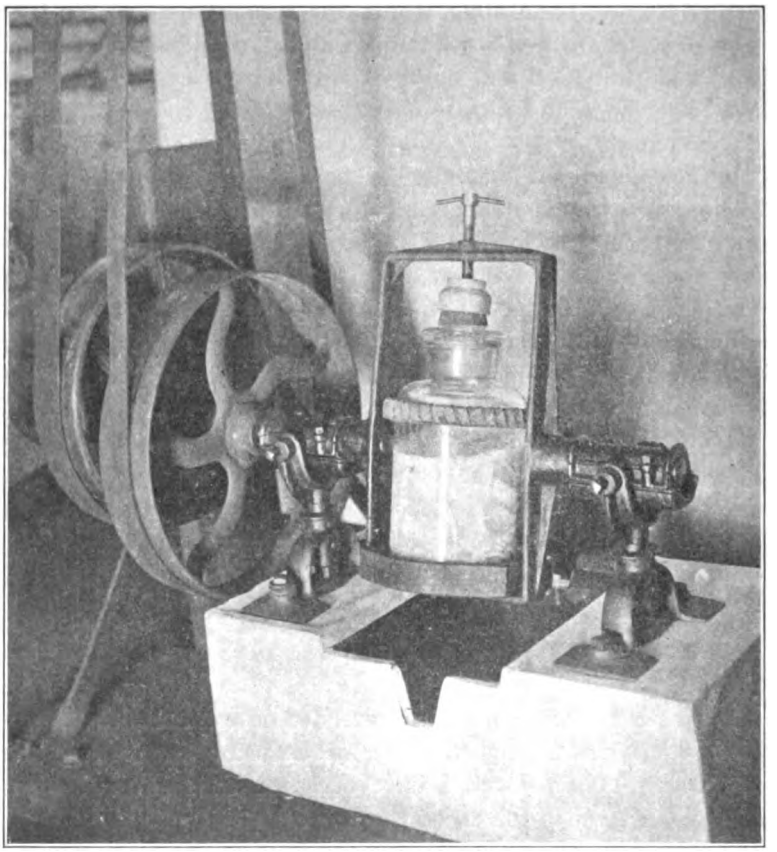
Having been called upon frequently to do work at our laboratory which necessitated the use of a drum larger than the regular non-tannin drum, I have designed and constructed the apparatus shown in the accompanying cut.

The frame is of cast iron, to the flat base of which is fastened the wooden socket which centers the bottle in the frame.

The bosses on either side of frame are fitted with 1 3/16 inch shafting so that the apparatus can be set up in standard hangers. We use a one-gallon glass stoppered bottle, but a much larger one may be used as the wooden sockets in the base of the frame are interchangeable.

The bottle is held in place by a screw in top of the frame fastened to a wooden cup containing a rubber stopper such as is used in the non-tannin shaker.

The agitator is perfectly balanced, easily cleansed and we find



for purposes such as processing hides for color tests, etc., that we get much better and quicker results than with a smaller drum. If there are any of our leather laboratory friends who should have occasion to install one of these machines, the pattern for the frame could be obtained from the writer.

NOTES ON EXTRACTION OF TANNING MATERIALS.

By George A. Kerr.

The recent effort of the A. L. C. A. to decide whether or not it should adopt an official form of extractor prompts me to submit the following notes relative to extraction, with the hope that some one who has the time to spare will continue the work and determine conclusively if the proper analysis of the liquor resulting from an extraction of spent or fresh tanning material will not tend to yield more comparative results than attempted control of the method of extraction in itself.

In the manufacture of tanning extracts, the writer has found it impossible to accurately check the results which obtain in practice with the analysis of the wood before and after leaching. That is to say, the yield of extract cannot be accurately determined by the difference between the indicated tannin or extractive contents of the wood previous to and after extraction in the mill.

The actual yield being in the majority of instances greater than that figured from analysis, led to the surmise, which subsequent observation tends to confirm, that the fault was in the laboratory.

It has probably been a matter of common observation that, when evaporation of the soluble solids from a spent wood or bark solution had reduced the volume to about one-fifth of the original 100 cc., a considerable precipitation occurred, and instead of the solution remaining clear until the evaporation was completed, the precipitation increased until in many instances a crust was formed, covering the entire surface of the solution.

Here we think we have found the chief cause of discrepancy between factory and laboratory figures, and it is not improbable it may be found to be an important cause of variation in the analysis of raw tanning materials, those which have been leached especially.

The presence of this precipitate makes it obvious that the extraction of spent wood and bark involves the extraction of considerable quantities of matter which is insoluble, excepting in extremely dilute solutions. Whether such matter is non-cellulose or the decomposition products of cellulose, we do not know, nor has its composition any important bearing on the point at this time.

It is evident, however, from the analysis and tests which are herewith submitted, that it is precipitated by hide powder, and therefore estimated as tannin, to a great extent, in spent wood or bark solutions, and because of its insolubility to a lesser extent in fresh wood or bark solutions, while in properly made concentrated liquors, it should not be present at all.

Illustrating the extent to which analysis is affected by this precipitable matter, extractions of ten samples of spent wood were made by our regular laboratory method, *i. e.*, the percolator. The period of extraction covered 5 hours. The quantity of wood used was 50 grams dry, and the volume of liquor taken off 1,000 cc.

A portion of liquor was analyzed in the usual manner (A in table) and 500 cc. of the remainder filtered and evaporated on the water bath until the volume was reduced to 100 cc. After cooling, the concentrated liquor was filtered, an aliquot portion measured off and diluted to the strength of the original solution. This liquor (B in table) was then analyzed in the same manner as the first portion.

Following are the figures thus obtained:

Column "A" is original liquor.

Column "B" is liquor after concentration and filtration.

Sample		Soluble Solids	Non-Tannin	Tannin
1	A	4.34	1.77	2.57
	B	3.79	1.72	2.07
2	A	2.51	1.29	1.22
	B	2.07	1.18	.89
3	A	2.62	1.32	1.30
	B	2.23	1.23	1.00
4	A	2.93	1.32	1.61
	B	2.46	1.21	1.25
5	A	3.73	2.07	1.66
	B	3.39	1.91	1.48
6	A	3.43	1.82	1.61
	B	2.88	1.73	1.15
7	A	2.28	1.45	.83
	B	2.01	1.38	.63
8	A	2.44	1.39	1.05
	B	2.10	1.23	.87
9	A	2.10	1.12	.98
	B	1.65	1.01	.64
10	A	2.21	1.08	1.13
	B	1.76	1.01	.75

The average soluble solids of these ten samples, as per "A," or

the usual analysis, is 2.85%. After concentration and filtration, the average figure for this item is reduced to 2.43%, showing a loss of 0.42%.

The average tannin figures are, in "A," 1.396% and "B," 1.073%, the difference being 0.323%.

The average non-tannin figures are not materially changed, the averages being respectively 1.46% and 1.36%, and the difference 0.1%.

It is apparent that at least three-fourths of the precipitated matter while in solution combines or is at least taken up by hide powder, while the original non-tannins are reduced to a very slight degree.

The extractions upon which the foregoing figures are based were made by the most moderate method which can be employed, excepting perhaps the Proctor percolator, and if such inaccuracy as to the available tannin can be introduced by it, is it not reasonable to suppose the drastic and long continued extraction as practiced when combined percolator and reflux extractors are used, will tend to aggravate the error?

Again, if five hours extraction with 1,000 cc. of water at 100°C. suffices to put into solution such difficultly soluble matter as this precipitate is found to be, does it not seem, the readily soluble tannin must be completely exhausted, previous to the solution of this matter, and therefore extended reflux extraction is not only a waste of time, but the means of making comparative results impossible?

Further, is it not reasonable to assume that if all liquors from spent wood or bark were concentrated to an extent sufficient to precipitate this substance and the liquor subsequently analyzed, the results would be more nearly comparative, under any conditions of extraction, except those which decompose tannin?

Aside from the question of extraction, it would seem the present provisional method of raw tanning material analysis as applied to spent materials gives results in which the soluble solids and tannin figures are so much too high as to vitiate their utility for factory control. For this reason, if for no other, the method needs revision.

It is not the idea of the writer to question the value of any

particular method of extraction, for although the evidence before him is scant, he is inclined to think any reasonable method is as good as another, provided this non-available matter is precipitated and filtered out of the liquor before analysis. We find the precipitated matter, after washing with cold distilled water, can be re-dissolved, but only after prolonged heating and in extremely dilute solutions. After re-dissolving, it does not give any precipitate with standard gelatine solution, unless it is acidified with acetic acid.

SOME UNSOLVED PROBLEMS IN LEATHER CHEMISTRY.[1]

By Prof. H. R. Procter.

The progress of the last twenty years in our knowledge of the chemistry of leather manufacture has been considerable, and every year becomes more rapid; but those who are actively engaged in the work are, perhaps more than others, aware that we are still at the beginnings of the science, and that what has been done should only be regarded as an encouragement to further progress, and as a step from which further advances must be made. It seems therefore appropriate in the first pages of a new technical journal to point out a few of the many directions in which our knowledge may be profitably advanced.

We have now got a method of technical tannin analysis, which at least in careful hands, stands on the same level of accuracy as most other technical analytical methods, and we cannot hope for very material progress along the same lines, though no doubt improvement in details is still possible. Even if some change in the direction of more complete separation of the tanning from the non-tanning substances were attainable, it is doubtful, considing the commercial difficulties which have arisen from the very slight change from the filter to the shake method, whether its introduction would be at present desirable; and I think we may assume that for a good many years to come, tanning materials will be bought on the basis of the shake method, though no doubt with increasing comprehension of the meaning of its results, and the varying practical value of one per cent. of tanning substance

[1] From *Leather*.

as derived from different materials. With the natural tanning materials, this knowledge is of course easily derived from experience, but with the continually increasing use of extracts, the necessity of chemical means of differentiating the tannins becomes urgent; and as yet it is only in the fewest cases that even the qualitative determination of the materials which have been used is practicable. It is not difficult to distinguish catechol tannins in mixture with pyrogallol derivatives, or *vice versa* (*e. g.* quebracho in oakwood, or myrabolams in quebracho); and a few materials, unfortunately usually the more valuable ones, contain substances with marked reactions, but tannins of the same class are so closely allied that their distinction in this way seems hopeless. It should, however, be possible in the future, as the chemistry of the tannins themselves is developed, to determine the leading constituents or their derivatives quantitatively; and even approximate methods of estimation of the catechol and pyrogallol tannins in a mixture would be of much value, and would often definitely decide whether an extract was what it professed to be. Especially is it desirable to be able to detect wood pulp liquors (so-called "pine wood extract") in other extracts, and the writer hopes to publish shortly some steps in this direction.

Turning from the tanning materials to the control of the tanning process itself, the two most important needs are the estimation of the free acid and of the tannin in the liquors. For the first of these, the limewater method has done good service, and in many cases is in regular use; and several other methods also give good comparative results, though none at present known is altogether satisfactory. The problem is more complex than it at first sight appears, since the liquors contain acids of all degrees of strength, down to the tannins themselves, and different indicators draw different lines as to what is to be reckoned and what is not, so that agreement cannot be expected. For the estimation of tannins the shake method gives results of fair accuracy, even in presence of the large amount of non-tannins in old liquors; but, though largely used in America for tannery control, it requires too much time and labor to be constantly employed, and a rapid direct volumetric method of fair

accuracy is wanted. The Löwenthal method with indigo and permanganate is still probably the best for this purpose, and with self-filling burettes, and a mechanical stirrer, estimations are very rapidly made. If chromed hide powder in the shake is used for detannization, a factor is easily obtained for comparison with the shake method by occasionally titrating the "total soluble" and "non-tannin" solutions; and for the control of liquors, detannizations may be made by using Dr. Paessler's dry chromed powder, or even chrome-leather shavings as suggested by Kopecky, without soaking or washing or allowance for added water; as small portions of salts, or even of soluble hide substances do not affect the Löwenthal test. In this way several liquors can be tested in an hour, with very close correspondence to shake-method results. There is no doubt that a proper relation of acid to tanning strength is of the greatest importance, not only in sole leather, but in dressing leather tannage; but our information is sadly deficient as to what the proper relation is in each case, and with varied materials. It is not merely in the first stages of sole leather tanning that acid is necessary; Bennett has recently shown, that with mimosa bark, which yields practically no natural acid, if used alone, it is necessary to add acid artificially, even in the layers, if firmness is to be maintained.

We have still very little precise information as to the causes and effects of swelling and falling of the hide, either in acid or alkaline solutions, though Stiasny's investigations on liming have shown that in the latter case not merely the alkalinity of the solution, but other unknown factors play their part, and that both practically and theoretically, it is important to distinguish between the swelling which increases the thickness of the hide, but leaves it soft, and the plumping under which it becomes tense and firm. In the first case, as in swelling by ammonia, increased solution of hide-substance seems to take place, hair is readily loosened, and a softer and lighter leather is produced, while in swelling in fresh limes, and still more in caustic soda, less waste of hide substance occurs, but hair is only slowly loosened. Of course both effects occur side by side and in all ordinary plumping processes both are combined in varying proportions.

So far, I have dealt only with practical questions of obvious

and immediate importance to our present processes, and if I go further some of my readers will be ready to blame me for wasting time on matters of purely theoretical and scientific interest; but I may suggest that while the former may lead to many detailed though valuable improvements, it is to the latter we must look for new departures and revolutionary changes; and I believe that, however unwelcome to the present-day manufacturer, such changes are bound to come. We have lived through the advent of chrome tannage and seen the effect it has had on the old style of leather manufacture, and it is not the last discovery which will come from the laboratory and upset the old trade.

While even 20 years back, we only knew of two or three substances, tannins, oils, and alum, which would make leather, it is now hard to say what will not make it; and among the scores of things known to the chemist to be capable of converting skin into leather, it is pretty certain that some will prove to be of commercial value. It is becoming more and more recognized by chemists that tanning is by no means a purely chemical process, but that the combination between tannin and gelatine is a colloid reaction. The very name is probably unfamiliar to most of my readers, and colloid chemistry is yet a science in the making, but it is one which is going to upset many preconceived notions with regard to tanning. Chemists have long divided substances into crystalloids, like sugar, salt and alum; and uncrystallizable ones like gelatine, tannins, gum and many mineral substances; and chemistry has concerned itself mainly with the former, which easily act on one another in comparatively simple ways. The uncrystallizable or colloid bodies have very little power of diffusion, and enter with difficulty into chemical reaction; hence the slowness of tanning with tannin compared to that with alum or chrome. It is now believed that the difference is not one of unchangeable nature, but of state; and even salt has been obtained in colloidal and uncrystalline form. We look upon gold as yellow and insoluble in water, but by appropriate treatment it can be obtained as a purple solution, possessing none of the ordinary characteristics of gold, but which can yet be shown to consist of actual metallic gold so finely divided that it remains permanently suspended in water, though a pinch of

salt will separate it as a blue powder. Iron or chrome oxide, equally insoluble under ordinary circumstances, can be obtained in a similar state, and capable of remaining in unaltered solution for an unlimited time. If, however, the iron and the gold solutions are mixed, they are mutually precipitated, leaving practically pure water; and it is believed that the tannin and the gelatine, both colloids, are precipitated in the same way. To obtain this precipitation, one of the colloids must possess acid, and the other basic properties, given often by a minute trace of one of the constituents of some salt which they absorb; and many bodies like gelatine are capable of taking either an acid or alkaline character according to the solution in which they exist. Hence probably the importance of a proper degree of acidity in tanning. Hence also, as a large number of bodies may be had in colloidal solution in water, and under proper conditions will produce colloidal precipitation, it is probable that almost an unlimited number of substances can be made to make leather.

ABSTRACTS.

The Determination of the Tensile Strength of Belting Leather. J. PAESSLER. *Ledertechnische Rundschau*, 1909, Nos. 1, 2; pp. 1-5, 9-13.—The usual requirements specify a minimum resistance to tearing of 3 kilos to 1 square millimetre cross-section. In measuring this, the amount of stretching during the test is also observed and expressed in percentage of total length subjected to tension. The test piece consists of a strip 30 m.m. wide, 100 m.m. long with an extension at each end of 40 m.m. width, 50 m.m. length which is clamped in the apparatus. The most accurate testing machines are of the hydraulic type, permitting a very gradual loading. For ordinary purposes, however, the testing machine of Fecken-Kirfel, Aachen, suffices and was used in the experiments here described, at the Freiberg station.

The writer finds that the results depend very much upon what part of the hide is taken for testing; the usual practice of taking a sample at random, without system, assuming that the strength depends wholly upon the tannage, is false; variations of 100 per cent. are thus obtained. The only systematic researches in this direction have been made by Bach and by Rudeloff. Bach found that the resistance increased from the tail towards the head of the animal. Rudeloff found that moisture increased the resistance, especially in chrome leathers, and recommended that comparative tests should be made only on leather which had been previously stored a week in a room of constant humidity. This was done in the experiments described below.

The material used in these investigations was furnished by the Belting Leather Manufacturers' Union of Rhineland and Westphalia. Thirty-eight leathers in all were examined, representing varied tannages, in most cases both unstretched leather and wet stretched. Strips were cut from each croupon at distances of 50, 350 and 500 m.m. from the middle line of the back, both right and left. Two test pieces were taken from each strip, at the neck and rump, making 12 tests in all from each croupon.

In a critical analysis of the detailed experimental data, it was found that the results varied greatly in different parts of the same croupon. On the whole the figures were the same, right or left. The neckpieces, with but one exception, gave greater resistance than the rump, the average resistances being 3.19 K. and 2.65 K. These results confirm the statement of Bach above referred to. At the end of the researches, some additional tests were made upon middle pieces taken between the neck and rump with 5 of the croupons. It was found that the resistance in most cases was greatest, the average figures being, neck, 2.9 K.; middle, 3.4 K.; rump, 2.7 K.

(To Be Continued.)

The Determination of Water in Fats and Oils. C. STIEPEL. *Siefensiederzeitung*, 1908 [35], 886.—The usual method may occasion a loss by oxidation during heating and a loss of volatile acids. These errors are avoided by passing a current of CO_2 into the assay flask which is heated on an air-bath, and by further attaching to the flask an absorption tube filled with water; this absorbs the expelled volatile acids which are afterwards titrated and allowed for.

Examination of Leather. (Anonym.) *Gummi Zeitung*, 1908, pp. 1151, 1178, 1199, 1264, 1319.—At the present time when so much embellished and weighted leather is on the market, it is indispensable for the consumer to test his ware. An addition of fat to vegetable tanned leather is essential to a certain extent; when extended to loading, the leather still increases in resistance, but in course of time some fat works out. The normal ash of vegetable tanned leather is from 0.3 to 2 per cent.; with imperfect deliming it may rise to 4 per cent., or more when sulphuric acid is used. Chrome tanned leather may give an ash of 10 to 15 per cent. without fraudulent loading. Leather which contains much unfixed tans is not waterproof and by washing, becomes porous and brittle. Pit-tanned leather contains 3 to 9 per cent. unfixed tans, leather weighted with extracts, 12 per cent. average. Artificial loading is also practiced with sugar, barium chloride and sulphate, salt, glycerine, starch, clay, etc. The soluble substances are added to the dried leather which absorbs them; the insoluble materials are added to the dressing. Barium sulphate is precipitated in the fibre by reaction of chloride with sulphuric acid.

Researches on Leather. NICOLARDOT, M. *Bull. Soc. d'Encouragement pour l'Industrie Nationale*, 1908, pp. 783-9.—For the determination of tensile strength, the samples of leather are taken longitudinally in the region

of the stomach, where the skin has the greatest resistance. The resistance of samples taken parallel to the spine is greater than of those cut in a perpendicular direction.

To determine water in leather, it is proposed to first extract the fats with chloroform and then dry in an oven at 110°. The author found that the method gave more water by 2 per cent. than by drying in the usual way in a vacuum for 48 hours.

The Rôle of Microbes in the Putrefaction of Hides. M. G. ABT. *Bull. du Syndicat général des Cuirs et Peaux de France*, reprint in *La Halle aux Cuirs*, 1908, No. 52, p. 837; 1909, Nos. 1, 2, 3; pp. 4, 18, 35.—Putrefaction is decomposition by microbes of very complicated nitrogenous bodies called proteins. The decompositions are gradual and in stages, producing simpler substances. Beginning with albumen, there are formed albuminoses, peptones, polypeptides and finally the crystalline acid amines and diamines which last may be considered as simple individuals. Putrefaction is then a protracted operation, requiring a certain time. Practically, there are three stages, liquefaction of the original substance, transformation into crystalloids, and lastly decomposition of these.

The microbes which take part in putrefaction are very numerous; nearly all require a nitrogenous nutrition which they derive from the substances they decompose. Some 30 to 40 have been described in the literature. In discussing hide, application is made of better studied putrefactions, such as that of meat and of oil-cake. Putrefactive microbes are divided into (1), proteolytic, which are capable of liquefying and then decomposing albumen, and (2), peptolytic, which are only capable of attacking products already very soluble, the peptones; they are inactive until the first class has commenced action. Another division is into simple ferments, capable of fermenting solely nitrogenous matter, and mixed ferments which act on carbohydrates, forming organic acids. Aerobes are those which need contact with oxygen to grow. Anaerobes derive their oxygen by reduction of the substance decomposed and cannot live in presence of free oxygen. The most important microbes are probably *B. putrificus* and *B. putidus gracilis*; they are anaerobes and live only in alkaline media. In a normal putrefaction, the different groups of microbes succeed each other quite regularly. At the outset, the aerobes produce acids; when the decomposition has proceeded to produce ammoniacal compounds the acids become gradually neutralized.

The Hide. The corium comprises soluble albumens contained in the vessels or conjunctive cells, the so-called interstitial substance, and the fibre. The liquid albumens, particularly the blood, are charged with microbes and ferment easily. The fibres on the contrary are very resistant to putrefaction. The interstitial substance is of great interest, being the seat of transformation. Reimer describes it under the name of coriine as an albuminoid, soluble in alkalies. Although its nature is not yet well known, it seems probable it should be considered as a product of decomposition of the fibre under the influence of alkalies.

In fact, Weiss, Procter, Wood and others have transformed isolated fibre completely into coriine by action of lime water. It follows that fresh hide does not contain coriine but that this is produced by putrefaction or in liming. It is eminently putrescible.

During soaking, all the soluble matter in the dried hide goes into solution; this is moderate in amount unless there has been a putrefaction before drying when the soluble matter will be much increased. All this soluble matter is liable to putrefaction not only in soaking, but in liming and bateing. It is not certain that all the microbes which may be isolated from the soaks, limes, bates and tan liquors are present in the original hide, but it is very probable. No doubt the microbes of the air and water, those attached to the walls of vats and those introduced by the bates, are of influence. The most important are those which remain in the pits and perpetuate themselves. Andreasch has isolated from tanning liquors the greater part of the putrefactive ferments known, excepting those which cannot live in presence of acids. Beginning with soaking, the development of microbes is limited by temperature, time and amount of dissolved nitrogenous substances. On coming into the limes the bacteria cease to multiply in the presence of alkali. But as the amount of dissolved hide increases, certain microbes develop. Passing to the dung bate, the hides are not in a condition favorable to putrefaction. Moreover, the bate is poor in nutritive material; Wood found in bates from pigeon dung, 0.2 per cent. solubles, from dog dung, 0.4 to 0.6 per cent., of which a large part has no nutritive value. The media commonly used in bacteriology contain at least 1 per cent. peptones, as well as other nutrients. In the bran bate, which is distinctly acid, the development of injurious microbes is arrested which might have begun in the dung bate. The greatest danger of putrefaction is in the soaks.

(To Be Continued.)

Fisetwood Extract. *Der Gerber*, 1909 [35], No. 826, p. 29.—This was formerly used only for dyeing alum leather, later chamois leather and now is much used for chrome leather. It is called in commerce also young fustic, Albanian or Hungarian yellow wood, being the root wood of the peruke bush (*Rhus cotinus*), growing in the countries south of the Alps. Its leaves also come into the market as Turkish sumac and serve for tanning or for dyeing silk. The yellow dye-stuff contained in the wood is fisetine similar to morine from genuine fustic; it is not free, but combined with tannin. It requires a mordant to develop and fix its color and is not therefore suited for vegetable tanned leather.

Fiset wood is not employed always to produce its own yellow color, but also to modify other dyes and to furnish a good ground for these. It is very useful in dyeing black with logwood or an acid aniline color. The dyeing of chrome leather is, in general, difficult because it is fat-liquored, which makes the color take unevenly. If the fat-liquoring follows the dyeing, the color is often partly extracted or changed Here

fiset is of great help, the leather being first treated with a decoction of the same, and then with the aniline color acid or direct aniline dyes are added in the same baths, basic dyes separately. For black chrome leather, the fiset decoction is mixed either with logwood dye or Direct Black (aniline dye).

Fiset wood is now much used in America and its exportation thither at times depletes the European market, especially as the production is irregular. Extracts of the wood are therefore in demand. These were formerly difficultly soluble and gave muddy liquors, spotting the leather. The writer has lately examined two brands of Fisetwood Extract, O and G, manufactured by Carl Feuerlein, Stuttgart, which do not have those defects, and give even better effects than liquors direct from the wood.

Observations on the Effect of Artificial Feedstuffs upon Hides and Skins. *Alfred Seymour-Jones.—Collegium,* 1909, No. 343, pp. 29-33.—The artificial feeding of cattle and sheep has increased greatly in recent times. Even in South America and Australia, the stock raisers feed with the oily grasses, etc., which yield the seeds producing the oil-cake used for feeding here at home. The result is that domestic hides are becoming much greasier than formerly. With sheep skins, fat is structurally present and when removed, leaves a hide which is more or less loose in substance. Within the last decade, a new form of looseness has appeared, confined to one or two places on the flesh side near the shoulder. Such skins are found after tanning to contain numerous small lumps on the grain which, on cutting, are found to contain a hard waxy fat. Such skins come from well-fed sheep, probably artificially fattened. Statistics show that the amount of oil-cake imported into Great Britain has in recent years much increased and most of this undoubtedly goes towards fattening cattle and sheep.

Belt Lacing Leather. W. EITNER. *Der Gerber,* 1909 [35], Nos. 824, 825; pp. 1, 15.—Special softness and flexibility are here required, together with great resistance to tearing. Formerly such lacings were cut exclusively from alum or alum-fat tanned leather. These possessed the above named properties, but the alum tanned leather was found in time to become brittle, due to its content of excess of alum and salt. The alum-fat tanned leather gave better results. After the alum tannage and removal of the excess of salts with luke-warm water, the leather is milled with a second water containing 5 per cent. chalk in order to neutralize the acid. The leather is then dried somewhat, and milled in a heated drum with a mixture of 3 parts tallow, 1 part fish oil, best applied in two successive stages, the total greasing amounting to 16 per cent. the weight of the alum leather. The greasing may be accomplished more rapidly and thoroughly with a fat liquor; a thorough neutralizing of the acid with chalk is here essential. The fat mixture (20 per cent. the weight of leather) consists of 12 per cent. tallow, 4 per cent. whale oil, 4 per cent. liquor soap. Combined tannage is sometimes used to give the leather a

desirable color. A preliminary tannage with gambier is followed by the usual alum tannage, employing first, a used liquor from a previous tannage and strengthening after a day or two. The drum may also be used, but does not give so good a color.

Transparent leather, which is no real leather, but hide impregnated with glycerine, was used to some extent. It was found to possess great strength, but became hard with time. Neither alum leather or transparent leather withstand the heat resulting from the friction in use.

Chrome tanned leather does not possess the defects of the above described leathers to such an extent. An account is given of the American manufacture taken from *Hide and Leather.*

Cut lacings are sometimes demanded with specially hardened tips. Alum tanned leather is easily hardened by dipping in water of 80°C., which extracts the alum and hardens the leather by heat; this process is hastened by adding 2 per cent. of acetic acid. Chrome tanned leather is not hardened so quickly; the tips are first dipped in benzine to extract fat, then dried, and next left several hours in 4 per cent. sulphuric acid, followed by water of 80° and stretching to dry.

School of the Tanner (*continued*); **De-Liming.** A. SCHMIDT. *Le Cuir*, 1909 [2], No. 2, p. 15.—Much more attention is given to this operation than formerly when the mechanical operations and washing were thought sufficient in most cases. The substances used in de-liming may be divided into four classes: acids which neutralize the lime, dung bates which neutralize the lime but also act upon the hide, making it come down, bran bates in which this action is increased, the hide even being attacked, and lastly, combined baths from the above. Formerly the sour liquors were used for de-liming. This is still a good method but must be rationally conducted. The tanner generally does not know how much acid is present nor the quantity of lime remaining in the hide. Moreover if the hide remain a long time in the liquor for the sake of ensuring complete de-liming and plumping, a fermentation may develop very injurious to the skin. This is more to be feared when there is but little tannin present to protect the hide. In making heavy leather where the appearance of the grain is not much considered, it does not harm if some lime remain in the leather. With smooth leather, it is different and here complete de-liming is striven for. This permits a rapid tannage, without which it is brittle and of defective color. With specially prepared acid solutions, mineral or organic, the de-liming may be perfectly regulated and carried out regularly without danger of the hide being attacked by microbes, as with old tan liquors. Sulphuric acid is much used for this purpose, but is distrusted because of its injurious action upon leather. When once fixed in the leather, it cannot be wholly removed by washing. However, if the washing is done carefully, the small amount remaining will not deteriorate the leather for several years and may be permitted in the case of sole leather, which is sooner used up in wear.

The Currying of Leather. MAGYAR BÖRIPAR, through *Le Cuir*, 1909 [2], No. 2, p. 30.—The aim in currying is to make the leather water-proof and more supple. To render vegetable tanned leather supple, it is impregnated with fat; 12 per cent. for belting leather, 15 per cent. for saddlers' and upper leather, 18 to 25 per cent. for harness leather, are required to produce the effect. Commercial leathers, however, show very different proportions. Saddler's leather contains over 40 per cent. grease and upper leathers, 35 per cent. or more, because of weighting. It is to the interest of the tanner, however, not to push the currying too far, for the quality and appearance of the leather are injured. The springiness of many leathers is due to an excessive currying. Average proportions are

	Weak	Medium	Strong	Very strong
Belting leather	2–8	8–15	15–20	21 upw'd.
Saddlers' leather...	8–10	10–15	15–25	26 "
Upper leather	5–15	15–25	25–30	31 "

The best materials are marine oils, degras, tallow, bone oil, so-called horse oil, and wool grease. Fats which contain acids or foreign substances like resins are to be avoided and particularly fats which have tendency to absorb oxygen from the air, thereby drying or becoming rancid. The springiness of leather is often due to use of such fats. Solid fats in general produce better results, filling the pores better than liquids; the color is clearer and the fat is not so easily expelled. Good mixtures are: 2 parts fish oil, 1 part tallow; equal parts of tallow, fish oil and degras. To get the best results, the leather should be moist when curried. Milling is therefore necessary, with sufficient heat to keep the fat melted.

PATENTS.

Leather Product and Process for Making the Same. U. S. Patent No. 911,140. HUGH MACKAY, El Paso, Texas.—The process of treating sole leather, which consists in soaking it in water, partially drying the soaked leather, coating the grain side of the partially dried leather with linseed oil and allowing the oil to dry, preparing a bath containing Portland cement, borax and water, soaking the partially treated leather in said bath, again partially drying the leather and coating both sides of the leather with linseed oil.

Glue Tester. U. S. Patent No. 911,277. E. S. SMITH, Niagara Falls, N. Y.—An apparatus for measuring the strength of gelatinous substances, comprising a pressure chamber, one side of which is provided with a flexible elastic diaphragm, means for bringing one free surface of the gelatinous substance into contact with the diaphragm, means for generating pressure within the chamber, thereby expanding the diaphragm and displacing the gelatinous substance, means of measuring the amount of such displacement, and means for measuring the pressure.

Improvements in Leather Splitting Machines. French Patent No. 341,025. SOC. REILLY ET SON.

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COMMITTEE NOTICE

At the last meeting of the Council it was decided that every laboratory represented in the active membership of our Associa-

OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR TANNIN ANALYSIS.

I. Crude Materials.

(1) *Moisture Determination*:

Upon receipt of the sample, grind promptly and dry 10 grams in the manner and for the period specified for evaporation and drying in extract analysis.

(2) *Preparation of Sample for Extraction*:

Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(3) *Amount of Sample and Proportion of Water for Extraction*:

For fresh materials the amount of sample and proportion of water for extraction should be such as to give between .35-.45 gram tannin per 100 cc. of solution. For spent materials this proportion should be approximated as closely as practicable.

(4) *Extraction of Sample*:

Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued until a portion tested with gelatine salt solution fails to give a precipitate. At least 400 cc. of the first portions of extractive solution should be removed and not subjected to further heating. A thin layer of cotton must be used in order to prevent fine material passing over.

(5) *Analysis*:

After extraction and dilution, solutions must be heated to 80° C., and analysis conducted as per Official Methods for Extracts. In case of weaker dilutions than the Official Method specifies, the amount of hide powder must be reduced in proportion to the reduction of tannin.

Ten grams of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

II. Analysis of Extracts.

(6) *Amount and Dilution for Analysis*:

Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from .35-.45 gram tannin per 100 cc. of solution, dissolve in exactly 900 cc. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

(7) *Total Solids*:

Thoroughly mix solution, pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying."

(8) *Soluble Solids*:

To 1 gram of kaolin in a beaker add 75 cc. of solution; stir and pour on a 590 S. & S. 15 cm. plaited filter paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 cc. of solution to 20° C.; refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 cc. of filtrate, as per "Evaporation and Drying."

Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

(9) *Non-Tannins*:

A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with twenty-five times its weight of water till thoroughly soaked. Add three per cent of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press, if necessary, so that the wet hide will contain between 70 and 75 per cent of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc. of the original solution such quantity of the wet hide as represents from 12 to 13 grams dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams kaolin to

the filtrate, stir and filter through folded filter (No. 1F Swedish, recommended) of size sufficient to hold entire filtrate, returning until clear. Evaporate 100 cc. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Note.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dried powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 per cent to 75 per cent water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

The non-tannin filtrate must not give a precipitate with a 1 per cent gelatine 10 per cent salt solution.

(10) *Tannin*:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

III. Analysis of Liquors.

(11) *Dilution*:

Liquors must be diluted for analysis so as to give as nearly as possible .7 gram solids per 100 cc. of solution.

(12) *Total Solids*:

To be determined as in Extract Analysis.

(13) *Soluble Solids*:

To be determined as in Extract Analysis.

(14) *Non-Tannins*:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing 70 per cent to 75 per cent moisture, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry hide powder per 200 cc.
.35——.45 gram.	8——10 grams.
.25——.35 gram.	5—— 8 grams.
.15——.25 gram.	2—— 5 grams.
.00——.15 gram.	0—— 2 grams.

Solutions to be shaken for non-tannins as in Extract Analysis; 100 cc. must be evaporated as in Extract Analysis.

IV. Evaporation and Drying.

(15) *Evaporation and Temperature*:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(16) *Dishes*:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor greater than 3 inches in diameter.

V. Determination of Total Acidity of Liquors.

(17) *Place 100 cc. of the Liquor in a 500 cc. Flask and Make up to the Mark with Water.*

To 100 cc. of diluted liquor in a flask with tube condenser, add 2 grams of chemically pure animal charcoal. Heat to boiling temperature with frequent shaking, cool, filter and titrate an aliquot portion with decinormal alkali.

On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

PROVISIONAL METHODS FOR SAMPLING TANNING MATERIALS.

(1) *Liquid Extract in Barrels*:

Samples to be taken at a temperature of 40° F. minimum from 10 per cent of the packages, as near as possible, by means of sampling tube which shall enter the bung and extend to at least the center of the barrel. These samples to be thoroughly mixed, using due precautions to prevent evaporation, and a composite sample of at least 4 oz., in duplicate, removed, sealed and labeled, with date of sampling, name of material, invoice number, or other means of identification.

(2) *Liquid Extract in Bulk*:

Extract shall be thoroughly plunged and sampled by passing a sampling tube to the bottom, through at least five sectors of contents, samples to be mixed thoroughly and composite samples drawn, sealed and labeled as in liquid extract in barrels.

(3) *Liquid Extract in Tank Cars*:

a. Where tank car extract is unloaded without the use of direct steam, into an empty container, the method of sampling is

to be the same as for liquid extract in bulk, the sample being taken from the container after the car is unloaded.

b. Tank cars unloaded without the use of direct steam shall be sampled by taking at least five pint samples of the extract as it flows from the car. One of these samples to be taken about 3 minutes after starting to unload, one to be taken about 3 minutes before unloading is completed, and other three samples to be taken at equal intervals between the first and last. These samples to be mixed and composite samples taken, sealed and labeled as usual.

Or, in case direct steam is used in unloading a tank car, shipment may be sampled according to the methods of sampling the liquid extract in bulk, the samples being taken directly from the car.

(4) *Solid Extracts*:

Solid extracts shall be sampled by taking a section from the center of the package to the surface after the removal of the cover. Samples as taken shall be immediately placed in clean, dry, closed receptacles, and when sampling is completed, broken, thoroughly mixed and duplicate samples of at least 6 oz. placed in clean, dry, glass receptacles, sealed and properly labeled. Sampling at place of manufacture shall be conducted by running portion from middle of strike into a mould holding at least two pounds, and immediately after cooling, selecting samples for analysis by method given above.

In lots of 300 bags or 100 barrels or less, at least 5 per cent of the bags or barrels shall be selected for sampling. On lots of 301 to 2,000 bags or 101 to 700 barrels, 3 per cent shall be sampled. On lots of more than 2,000 bags or 700 barrels, 1 per cent shall be sampled.

Where a considerable period of time elapses between the sampling and analysis of sample, the latter should be weighed on day of sampling, and certified weight should appear on label.

(5) *Crude Tanning Materials*:

Shipments in bags, mats or barrels, of barks, nuts, beans, fruits, leaves (ground and unground), roots and ground wood, are to be sampled by opening each of the packages chosen for sampling and selecting an equal portion therefrom. These samples to be

mixed and composite samples of the required amount taken and labeled as usual. In lots of 20 tons or less, 5 per cent of the packages shall be sampled. In lots of above 20 tons up to 101 tons, 3 per cent shall be sampled. In lots of 101 tons or more, 1 per cent of the packages shall be selected for sampling.

(6) *Crude Tanning Materials in Bulk*:

a. Barks, Nuts, Beans, Pods, Ground Materials, etc.

Equal portions shall be selected from at least five parts of the lot, mixed, sealed, and labeled in duplicate.

b. Wood.

Billets or logs shall be selected from at least five parts of the lot, and the sawdust obtained by sawing completely through each billet or log selected, thoroughly mixed, sealed and labeled in duplicate.

(7) *Sampling of Spent Tan and Spent Wood*:

Spent tan and wood samples should be taken from the top, middle and bottom of a spent leach, and placed in a covered pail, contents of pail to be stored in a covered barrel to be kept for the desired period. When a laboratory sample is desired, thoroughly mix contents of the barrel and dry a portion over steam pipes in a location free from bark dust. The dry laboratory samples should be at least 10 oz.

(8) *Ground Barks and Cut Woods*:

These samples should be taken at intervals as the ground material enters the leach. Composite samples shall be made up from these samples and shall be submitted undried to the laboratory.

(9) *Liquor Samples*:

Routine samples shall be taken by plunging the liquor and removing a pint and storing in earthenware crocks, having earthenware lids. The samples should be of the same size and taken under exactly similar conditions. The storage of crocks should be located where the temperature averages between 40° and 70° F. For the laboratory sample plunge the crocks well and fill a pint bottle nearly full, seal and label with required data.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state

both upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the provisional method of sampling of The American Leather Chemists Association."

The above has been adopted as the provisional method of this Association and each and every member of the Association, when called upon to do official sampling, is requested to sample according to this method.

PROVISIONAL METHOD FOR LEATHER ANALYSIS.

(1) *Preparation of Sample*:

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) *Moisture*:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) *Fats*:

Extract 5 to 10 grams of air-dried leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

(4) *Ash*:

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) *Water-Soluble Material*:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for three hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) *Glucose*:

To 500 cc. of the solution obtained by extraction according to Par. 4, add 20 cc. of lead sub-acetate, shake well, let stand for an hour and filter. To 400 cc. of filtrate add dry Na_2CO_3 and

filter. To the filtrate add 5 cc. concentrated HCl and boil for two hours, allowing the solution to evaporate to about 90 cc. Add dry Na_2CO_3 until the solution is about neutral, make up to 100 cc. and filter if necessary.

Take an aliquot part containing not more than .25 gram of sugars, add to 60 cc. of Allihn's Fehling's solution, dilute with water to 145 cc. if necessary, cover with a watch glass, bring to boil and set in a boiling water bath for exactly 30 minutes. Filter through an asbestos mat in Gooch crucible, wash with hot water to free from soluble salts and finally with alcohol, dry 1 hour in water oven, cool and weigh. Multiply the weight of cuprous oxide by .8883 and calculate to glucose according to the following table:

TABLE FOR THE DETERMINATION OF THE GLUCOSE IN TANNING MATERIALS THROUGH THE COPPER WEIGHED, AFTER HEATING FEHLING'S SOLUTION WITH THE GLUCOSE SOLUTION FOR HALF AN HOUR.

R. Koch and R. Ruhsam (*J. S. C. I.*, 13, 1227, *et. seq.*)

Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.
1	0.4	25	10.3	49	20.7
2	0.8	26	10.7	50	21.3
3	1.2	27	11.1	51	21.8
4	1.6	28	11.6	52	22.3
5	2.0	29	12.0	53	22.8
6	2.5	30	12.4	54	23.3
7	2.9	31	12.9	55	23.9
8	3.3	32	13.3	56	24.4
9	3.7	33	13.7	57	24.9
10	4.1	34	14.1	58	25.4
11	4.5	35	14.6	59	25.9
12	4.9	36	15.0	60	26.4
13	5.3	37	15.4	61	26.9
14	5.7	38	15.9	62	27.4
15	6.1	39	16.3	63	28.0
16	6.5	40	16.7	64	28.5
17	7.0	41	17.2	65	29.0
18	7.4	42	17.6	66	29 5
19	7.8	43	18.0	67	30.0
20	8.2	44	18.4	68	30.5
21	8.6	45	18.9	69	31.0
22	9.0	46	19.3	70	31.6
23	9.4	47	19.7	71	32.1
24	9.9	48	20.2	72	32.6

Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.
73	33.1	120	57.2	167	80.5
74	33.6	121	57.7	168	81.0
75	34.1	122	58.2	169	81.4
76	34.6	123	58.7	170	81.9
77	35.1	124	59.2	171	82.4
78	35.7	125	59.7	172	82.9
79	36.2	126	60.2	173	83.4
80	36.7	127	60.7	174	83.9
81	37.2	128	61.2	175	84.4
82	37.7	129	61.7	176	84.9
83	38.2	130	62.2	177	85.4
84	38.7	131	62.6	178	85.9
85	39.2	132	63.1	179	86.4
86	39.8	133	63.6	180	86.9
87	40.3	134	64.1	181	87.4
88	40.8	135	64.6	182	87.9
89	41.3	136	65.1	183	88.4
90	41.8	137	65.6	184	88.9
91	42.3	138	66.1	185	89.4
92	42.8	139	66.6	186	89.9
93	43.3	140	67.1	187	90.4
94	43.9	141	67.6	188	90.9
95	44.4	142	68.1	189	91.3
96	44.9	143	68.6	190	91.8
97	45.4	144	69.1	191	92.3
98	45.9	145	69.6	192	92.8
99	46.4	146	70.1	193	93.3
100	46.9	147	70.6	194	93.8
101	47.5	148	71.1	195	94.3
102	48.0	149	71.5	196	94.8
103	48.5	150	72.0	197	95.3
104	49.0	151	72.5	198	95.8
105	49.5	152	73.0	199	96.3
106	50.0	153	73.5	200	96.8
107	50.5	154	74.0	201	97.3
108	51.0	155	74.5	202	97.8
109	51.6	156	75.0	203	98.3
110	52.1	157	75.5	204	98.8
111	52.6	158	76.0	205	99.3
112	53.1	159	76.5	206	99.8
113	53.6	160	77.0	207	100.3
114	54.1	161	77.5	208	100.8
115	54.6	162	78.0	209	101.4
116	55.1	163	78.5	210	101.9
117	55.7	164	79.0	211	102.4
118	56.2	165	79.5	212	102.9
119	56.7	166	80.0	213	103.5

Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.
214	104.0	260	128.0	306	152.2
215	104.5	261	128.5	307	152.8
216	105.0	262	129.0	308	153.3
217	105.5	263	129.5	309	153.9
218	106.0	264	130.1	310	154.4
219	106.6	265	130.6	311	155.0
220	107.1	266	131.1	312	155.5
221	107.6	267	131.6	313	156.0
222	108.1	268	132.2	314	156.5
223	108.7	269	132.7	315	157.1
224	109.2	270	133.2	316	157.6
225	109.7	271	133.7	317	158.1
226	110.2	272	134.2	318	158.7
227	110.7	273	134.7	319	159.2
228	111.2	274	135.3	320	159.8
229	111.8	275	135.8	321	160.3
230	112.3	276	136.3	322	160.9
231	112.8	277	136.8	323	161.4
232	113.3	278	137.4	324	162.0
233	113.8	279	137.9	325	162.5
234	114.4	280	138.4	326	163.0
235	114.9	281	139.0	327	163.6
236	115.4	282	139.5	328	164.1
237	115.9	283	140.0	329	164.7
238	116.4	284	140.5	330	165.2
239	117.0	285	141.1	331	165.8
240	117.5	286	141.6	332	166.3
241	118.0	287	142.1	333	166.9
242	118.5	288	142.6	334	167.4
243	119.0	289	143.2	335	167.9
244	119.5	290	143.7	336	168.4
245	120.1	291	144.2	337	169.0
246	120.6	292	144.7	338	169.5
247	121.1	293	145.3	339	170.1
248	121.6	294	145.8	340	170.6
249	122.1	295	146.3	341	171.2
250	122.7	296	146.9	342	171.7
251	123.2	297	147.4	343	172.2
252	123.7	298	147.9	344	172.8
253	124.2	299	148.4	345	173.3
254	124.8	300	149.0	346	173.9
255	125.3	301	149.5	347	174.5
256	125.8	302	150.1	348	175.0
257	126.3	303	150.6	349	175.6
258	126.9	304	151.1	350	176.2
259	127.5	305	151.7	351	176.8

Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.	Cu. Mgrms.	Glucose Mgrms.
352	177.3	394	201.5	436	226.4
353	177.9	395	202.1	437	227.1
354	178.5	396	202.7	438	227.8
355	179.1	397	203.3	439	228.5
356	179.6	398	203.8	440	229.1
357	180.2	399	204.4	441	229.8
358	180.8	400	205.0	442	230.5
359	181.4	401	205.6	443	231.2
360	181.9	402	206.2	444	231.8
361	182.5	403	206.8	445	232.5
362	183.1	404	207.3	446	233.2
363	183.7	405	207.9	447	233.9
364	184.2	406	208.5	448	234.5
365	184.8	407	209.1	449	235.2
366	185.4	408	209.7	450	235.9
367	186.0	409	210.3	451	236.6
368	186.5	410	210.8	452	237.2
369	187.1	411	211.4	453	237.9
370	187.7	412	212.0	454	238.6
371	188.3	413	212.6	455	239.3
372	188.8	414	213.2	456	239.9
373	189.4	415	213.8	457	240.6
374	190.0	416	214.4	458	241.3
375	190.6	417	214.9	459	242.0
376	191.1	418	215.5	460	242.6
377	191.7	419	216.1	461	243.3
378	192.3	420	216.7	462	244.0
379	192.8	421	217.3	463	244.7
380	193.4	422	217.9	464	245.3
381	194.0	423	218.4	465	246.0
382	194.6	424	219.0	466	246.7
383	195.2	425	219.6	467	247.4
384	195.7	426	220.2	468	248.0
385	196.3	427	220.8	469	248.7
386	196.9	428	221.4	470	249.4
387	197.5	429	221.9	471	250.1
388	198.0	430	222.5	472	250.8
389	198.6	431	223.1	473	251.4
390	199.2	432	223.7	474	252.1
391	199.8	433	224.4	475	252.8
392	200.3	434	225.1	476	253.5
393	200.9	435	225.8		

(7) *Nitrogen*:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

Reagents.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acids against ammonium hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

Determination.

Place .7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid for from 5 to 15 minutes, or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150

cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1 hour and a half. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

PROVISIONAL METHODS FOR THE ANALYSIS OF OILS AND FATS.

Saponification Value.

Preparation of the Alcoholic KOH.—Purify the alcohol as follows: To ordinary alcohol add potassium permanganate in very fine powder or saturated solution until the pink color holds for about ten minutes; allow to stand over night, filter and distil over a fixed oil and sodium hydroxide, the first portions of the distillate, about a quarter, being rejected. Dissolve the KOH in the alcohol thus prepared, filter, and make up to half normal strength.

Determination.—Weigh off accurately in a flask holding 150-200 cc., 1.5-2.0 grams of the fat, or oil, purified and filtered if necessary. Next run into a flask 25 cc. of the alcoholic potash, attach a long cooling tube or invert condenser, and heat on the water bath for thirty minutes, frequently imparting a rotary motion to the contents of the flask until complete solution has been effected, which can always be done unless there is considerable unsaponifiable material present. After this allow to simmer, but not to boil vigorously, for the remainder of the time. Next add 1 cc. of a 1 per cent phenolphthalein solution (prepared by dissolving 1 gram phenolphthalein in 100 cc. 90 per cent alcohol) and titrate back the excess of potash with half-normal hydrochloric acid.

It is always best to make a blank test, treating the same amount of alcoholic potash in exactly the same manner as the solution of fat. Every source of error, as carbonic acid, etc., has therefore, as near as possible, the same influence on the final result, and is thus eliminated. The difference in the number of cubic centimeters of acid used for the blank test and the real test corresponds to the quantity of potash required, and is calculated to milligrams of potash to 1 gram of fat.

Acid Value.

Weigh accurately a convenient quantity of the material to be

tested into an Erlenmeyer flask, and treat with about 25 cc. of a mixture of alcohol and ether, previously rendered slightly pink with alcoholic KOH after the addition of 1 cc. 1 per cent phenolphthalein solution. Then titrate the mixture to the same point to which the solvent had been brought. Use tenth-normal alcoholic KOH for this and from the number of cubic centimeters required, calculate the amount of KOH absorbed. This expressed as the number of milligrams per gram of substance is the acid value.

Iodine Value.

A. O. A. C. Official Method—The Hanus Method.

Bulletin No. 107.

(a) *Preparation of Reagents—Hanus Iodine Solution.*—Dissolve 13.2 grams of iodine in 1000 cc. of glacial acetic acid (99.5 per cent) showing no reduction with bichromate and sulphuric acid; add enough bromine to double the halogen content determined by titration— 3 cc. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

Decinormal Sodium Thiosulphate Solution.—Dissolve 24.8 grams of chemically pure thiosulphate, freshly pulverized as finely as possible and dried between filter- or blotting-paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made.

Starch Paste.—Boil 1 gram of starch in 200 cc. of distilled water for ten minutes and cool to room temperature.

Solution of Potassium Iodide.—Dissolve 150 grams of potassium iodide in water and make up to 1 liter.

Decinormal Potassium Bichromate.—Dissolve 4.9083 grams of chemically pure potassium bichromate in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

(*b*) *Determination*—(1) *Standardizing the Sodium Thiosulphate Solution.*—Place 20 cc. of the potassium bichromate solution, to which has been added 10 cc. of the solution of potassium iodide in a glass-stoppered flask. Add to this 5 cc. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to

flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

(2) *Weighing the Sample.*—Weigh about 0.5 gram of fat or 0.250 gram of oil[1] on a small watch crystal or in some other suitable way. Melt the fat, mix thoroughly, pour onto the crystal and allow to cool. Introduce the watch crystal into a wide mouth 16-ounce bottle with ground glass stopper.

(3) *Absorption of Iodine in Hanus Method.*—Add 25 cc. of the iodine solution to the fat or oil dissolved in 10 cc. of chloroform. Allow to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60 per cent of the amount added.

(4) *Titration of the Unabsorbed Iodine.*—Add 10 cc. of the potassium iodide solution and shake thoroughly, then add 100 cc. of distilled water to the contents of the bottle, washing down any free iodine that may be noted on the stopper. Titrate the iodine with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

(5) *Standardizing the Iodine Solution by Thiosulphate Solution.*—At the time of adding the iodine solution to the fat employ two bottles of the same size as those used for the determination for conducting the operation described under paragraphs (3), (4) and (5), but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid and alcohol have very high coefficients

[1] Use from 0.100 to 0.200 gram in case of drying oils which have a very high absorbent power.

of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

Per cent of iodine absorbed:

Weight of fat taken	1.0479	grams
Quantity of iodine solution used	40.0	cc.
Thiosulphate equivalent to iodine used	62.1	cc.
Thiosulphate equivalent to remaining iodine	30.2	cc.
Thiosulphate equivalent to iodine absorbed	31.9	cc.
Per cent of iodine absorbed (31.9 × 0.012697 × 100) divided by 1.0479	38.65	

Unsaponifiable Matter.

Wherever possible use the following method: Saponify 5 grams, or its equivalent, with 5 cc. of a 50 per cent by volume aqueous KOH solution and 25 cc. alcohol. Heat on the water bath for half an hour, frequently agitating at the beginning until as complete solution has been effected as is possible. Then transfer to a shallow porcelain dish, using alcohol to rinse the flask. When the alcohol is about half evaporated off, mix 10 grams of sodium bicarbonate and 25 grams of clean quartz sand, previously washed with HCl and distilled water and dried thoroughly. Add this mixture to the soap and stir together with a glass rod. Evaporate to dryness and continue the drying for several hours or over night. The mixture is then pulverized and placed in a Soxhlet extraction apparatus, where it is extracted with a low-boiling petroleum ether for four or five hours. The other solution, containing the unsaponifiable matter is then transferred to a separatory funnel and washed with distilled water. Then filter into a tared flask, and distil off the solvent. The last traces may be removed by passing a current of air through the flask over the residue and finally drying in an oven at 98-100° C. for four hours. The residue is weighed as unsaponifiable matter.

For oils that cannot be treated in this way on account of their forming a glutinous mass with petroleum ether, proceed as follows:

Saponify in the same manner as above and transfer to a shallow porcelain dish. Evaporate to dryness and continue to dry for several hours, or over night, but without adding sand and sodium bicarbonate. Next add about 30 cc. petroleum ether and rub it up with the soap by means of a glass rod flattened at one

end. Then decant off the ether, with whatever soap may be in suspension in a finely divided condition and repeat the operation several times until the soap is thoroughly extracted. No less than 200 or 300 cc. in all should be used. The soap in suspension, as well as in solution is next washed out with distilled water in a separatory funnel, using a little alcohol to break up the emulsions. The washing should be proceeded with cautiously at first, and the clear ether transferred to another funnel as fast as it is formed, where it may be vigorously shaken. The aqueous soap solution should also be shaken out with petroleum ether as some of the unsaponifiable matter is apt to pass into the aqueous part together with the soap. When thoroughly washed, all the ether solutions are filtered into a tared flask, the solvent distilled off, the last traces being removed by passing a current of air through the flask and drying in the oven for four hours, as above. The residue, however, may contain small amounts of fatty acids which can be determined from the acidity and a correction made.

Maumene Test

In a tall 100 cc. beaker weigh out such a quantity of oil as when made up to 50 grams with mineral oil will not give a rise in temperature above 60° C. Make up to 50 grams with mineral oil and place in a large beaker well lined with hair. Add 10 cc. concentrated sulphuric acid of the same temperature as the oil mixture, taking one minute to add and always allowing the pipette to drain the same length of time. Stir constantly with the thermometer during the addition of acid and continue stirring until the temperature has reached the highest point. Run blank, using the same amount of mineral as for test. Deduct this rise from the total rise for the mixed oil. For specific temperature, run 50 grams of water in the same way as the sample was run. Divide the rise in temperature per gram of oil by rise in temperature per gram of water and multiply the result by 100.

Specific Gravity.

Specific gravity should be determined at 20° C., both the substance and the distilled water with which it is compared being at that temperature.

Titer Test—Provisional.

A. O. A. C. Provisional Method.

Bulletin No. 107.

(*a*) *Standard Thermometer.*—The thermometer must be graduated in tenth degrees from 10° to 60°, with a zero mark, and having an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about fifteen inches over all. The thermometer is annealed for seventy-five hours at 450° C. and the bulb is of Jena normal 16-inch glass, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched on the stem, the graduation to be clear cut and distinct but quite fine.

(*b*) *Determination.*—Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent by volume alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used boil for 40 minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent sulphuric acid (25° Baumeé) to free the fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1×4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8×6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.10°

C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test tube and add 15 cc. of alcohol (95 per cent by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

Melting-Point.

Take a tube of thin glass 2½ inches in length, and of such size that when the thermometer is inserted there will be about 1 mm. space between it and the glass. Fuse one end of the tube in the flame until the edges are drawn in slightly, forming a smooth, round hole. About half an inch from the other end make a small hole, either by fusing and blowing, or by filing. The tube is then ready for use. Draw a rubber band tightly over the end that was partially closed by fusion and bind on with a rubber ring. Pour such a quantity of the melted fat into the tube that when the thermometer is inserted the bulb will be a little more than covered by fat. The column of fat should then be about one and one-fourth inch in height. The thermometer, which is inserted to near the bottom of the tube is firmly secured with a perforated cork. The fat is now cooled well down below its melting-point by immersing in cold water. When this is done, take the apparatus from the cold water, remove the rubber band, and wipe dry. Then suspend the thermometer with the tube and fat attached, in an Erlenmeyer flask, or other convenient air bath, securing it by means of a cork. Place on a water bath and as the temperature slowly rises note the point at which the fat begins to protrude quite perceptibly, also the point at which the first drop falls and the point at which the fat becomes clear. For the latter, a small cork is inserted to prevent the fat from running out. Then remove the cork, and as the fat runs out notice its consistency, whether thin or viscous.

Cold Test—Millwood.

Warm the oil until the stearine is dissolved and filter, through several thicknesses of filter paper, into a *dry* 4-ounce wide-mouth bottle, 1½ ounces of the oil to be tested; place in a freezing mixture and stir until the oil becomes solid, then cork and leave for one hour in the freezing mixture. Take the bottle from the freezing mixture, wipe it dry, and place in a holder of ordinary magnesia, asbestos pipe covering, or any suitable holder which will insulate the sides of the bottle. The frozen oil is broken up and well stirred with the thermometer, and at every degree rise in the temperature the bottle is inverted; continue until the oil will run to the other end of the bottle. The temperature registered at this stage is to be considered the cold test.

Cloud Test—Manns.

(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding point is reached.

(2) The oil must be heated to 150° C. over a free flame, immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice and water. The test is conducted as follows: the oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety, the oil is transferred to a 4-ounce bottle, which must be perfectly dry. One and one-half ounces of the oil are sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few minutes. The oil must not be allowed to chill on the sides and bottom of the bottle.

This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the dry body of the oil, the temperature at which this cloud occurs is noted.

With care, results concordant to within 1 degree Fahrenheit can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit. The oil must be tested within a short time after heating to 150° C., and a re-test must always be preceded by reheating to that temperature. The cloud point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

THE EFFECT OF ILLUMINATING GAS ON LEATHER.

In connection with a series of experiments on the influence of sulphur in illuminating gas, Mr. Arthur D. Little, chemical expert and engineer, Boston, had occasion to report upon its effect on leather. He says that "there has been considerable agitation in England on account of the deterioration of leather book bindings in many of the libraries. A special committee was appointed from the Society for the Encouragement of Arts, Manufacture and Commerce to inquire into the reasons for the deterioration of leather books. A sub-committee reported that as a result of the experiments which had been undertaken they were of the opinion that of the deleterious influences to which books are subjected, the fumes of burned gas are the most fatal, owing no doubt to the sulphuric and sulphurous acids which they contain.

Professor J. Gordon Parker, a well-known English leather chemist, testified before the Board of Trade Committee in 1904 that he carried out numerous experiments exposing leather to the fumes of burning gas and found that these fumes rotted the leather so that in time it was absolutely destroyed and crumbled to a powder. He found moreover that the leather under these conditions contained sulphuric acid. It developed on questioning Dr. Parker that sulphuric acid is used in the bleaching and dyeing of leather, and that if once used it cannot be successfully

washed out. On that account much of the modern leather in books will go to pieces anyway. The leather which Professor Parker used for his experiments, however, was especially prepared by himself, and was free from any mineral acids. He was very emphatically of the opinion that the amount of sulphur in gas was of great importance in respect to the durability of leather. It was pointed out at the time, however, that in special libraries where considerable quantities of leather bound books were kept, arrangements might easily be made to light with electricity or oil. It also developed in the inquiry that Professor Parker's experiments on leather bound books were carried out in a very small, air-tight room where a large amount of gas was burned under conditions which caused a precipitation of moisture on the sides of the room and on the leather, and that this moisture would of course contain sulphuric acid. The conditions of his experiments were very far from those of an ordinary library, and it is questionable if, under modern methods of lighting, where very much smaller quantities of gas are used in incandescent mantles, and in rooms where there is any kind of ventilation whatever, the action of the products of combustion of illuminating gas on books is, to say the least, not proven.

Mr. Little points out as demonstrating the relative insignificance of the question of sulphur in gas as a possible factor in the deterioration of leather that practically all light weight leathers now go through the process of "chrome tanning." He refers particularly to the Schultz process, in which the skins coming from the beam house are first soaked in a solution of bichromate of potash, and after this has thoroughly penetrated the tissue, the skin is removed to a bath of hyposulphite of soda, to which later a mineral acid, usually muriatic acid, is added to decompose the hyposulphite, with evolution of sulphurous acid gas and precipitation of sulphur in the minutely divided form in the bath and throughout the skin, the object of the reaction being the reduction of the chromic acid of the bichromate to chromic oxide, which renders the gelatin of the skin insoluble and thereby converts it into leather. A considerable proportion of the sulphur precipitated during the reaction is necessarily left within the substance of the skin in a form of extremely minute subdivisions, in which form of course the surface presented to

oxidation is relatively very great, so that under appropriate conditions, especially as to moisture, a slow oxidation of the sulphur to sulphuric acid is to be expected. That these leathers in fact so seldom deteriorate in use is due merely to the general absence of conditions favorable for this oxidation. It can however be confidently asserted that the danger from deterioration through oxidation of the sulphur already within the leather is so incomparably greater than that likely to result from any sulphur compounds derived from gas burned in the vicinity of the leather, as to render this last named cause a practically negligible one.

A METHOD FOR THE ESTIMATION OF NITROGEN IN ORGANIC SUBSTANCES.[1]

By Hugh Garner Bennett.

The Kjeldahl process of nitrogen estimation is open to several sources of error, and numerous forms of apparatus have been devised to carry it out with the maximum convenience, accuracy, and speed. The great advantage of the process now suggested is that no such apparatus is at all necessary, the whole operation being conducted in one flask.

It is some years since the reaction between ammonia and formaldehyde to form hexamethylenetetramine was first employed as a means of estimating the latter, but it is only recently that the same reaction has been utilized for the estimation of ammonia. It has been shown, however, that if a formaldehyde solution be added to an ammonium salt, the formation of hexamethylenetetramine takes place as usual, and the acid combined with the ammonia remains as free acid, and can be titrated (Ronchèse, J. Pharm. Chim., 1907 (VI.), 25, 611-617). It is now suggested, therefore, that this process of ammonia estimation should be combined with the Kjeldahl method of digesting with sulphuric acid, for the estimation of nitrogen in organic substances.

The substance under examination is digested as usual with sulphuric acid until the liquor is clear, and the excess of acid

[1] From the *J. S. C. I.*

carefully neutralized by adding a solution of caustic soda until a pink color is obtained with phenolphthalein. A neutral solution of formaldehyde is then added, liberating the sulphuric acid present as ammonium sulphate, according the equation:—

$$2(NH_4)_2SO_4 + 6H.CHO =$$
$$2H_2SO_4 + N(CH_2.N:CH_2)_3 + 6H_2O.$$

Hexamethylenetetramine is quite neutral to phenolphthalein and the liberated sulphuric acid is then titrated with N/10 sodium hydroxide solution until the pink color returns. From the amount of N/10 alkali used, the amount of ammonia originally present as ammonium sulphate, and hence also the amount of nitrogen present in the substance under examination can easily be determined.

This mode of procedure has been found very convenient for the estimation of hide-substance in leathers, one of the most important determinations in leather analysis. From 0.4 to 0.5 grm. of leather is accurately weighed out into a Jena flask of about 500 c.c. capacity and digested over a small flame with 15 c.c. of concentrated sulphuric acid until clear. The liquor in the flask is then carefully neutralized to phenolphthalein; a 50 per cent. solution of soda is used until the solution is nearly neutral, and the neutralization then completed with N/10 sodium hydroxide. The formaldehyde solution (25 c.c. of about 40 per pent. strength) is now added to the flask, and after mixing well the liquor is titrated with N/10 caustic soda until a permanent pink is obtained. Each c.c. of N/10 alkali required corresponds to 0.0017 grm. of ammonia or 0.0014 grm. of nitrogen, or 0.00786 grm. of hide-substance, as hide-substance contains 17.8 per cent of nitrogen. Commercial solutions of formaldehyde are usually slightly acid, and of course must be made neutral before adding to the flask. This may be done by neutralizing to phenolphthalein with standard caustic soda, or by shaking the solution up with barium carbonate and allowing it to stand overnight. The following results were obtained with leathers treated with this process and with the ordinary Kjeldahl process:—

No. of leather sample employed	Percentage of nitrogen found	
	Formaldehyde method	Kjeldahl method
1	12.20	12.20
2	12.50	12.48
3	12.20	12.20
4	14.70	14.68
5	14.90	14.90
6	12.08	12.12
7	12.21	12.19
8	11.64	11.61
9	13.25	13.24
10	11.67	11.65
11	12.40	12.40

In applying the process for the estimation of dissolved hide-substance in soak liquors and lime liquors, 100 c.c. of the filtered liquor is pipetted into the Jena flask, made distinctly acid with sulphuric acid, evaporated to small bulk, and then digested with concentrated sulphuric acid and titrated as before. The following results have been obtained with a series of tannery lime liquors:—

Liquor	Mgrms. of nitrogen per 100 cc. liquor	
	Formaldehyde method	Kjeldahl method
1	15.68	15.68
2	42.00	41.90
3	45.36	45.29
4	19.88	19.80
5	50.96	50.96
6	12.60	12.51
7	42.00	41.85

The amount of hide-substance which has gone into solution is usually calculated on the assumption that 17.8 grms. of nitrogen correspond to 100 parts of dissolved hide-substance.

It is of course conceivable that in certain cases some complication may arise which will prevent the successful use of this method. One such case has come under the author's notice. In determining the nitrogenous matter in silk by both Kjeldahl and formaldehyde methods, the following results were obtained:—

Sample	Percentage of nitrogen	
	Formaldehyde method	Kjeldahl method
Black silk	(1) 7.4	(1) 8.7
	(2) 7.4	(2) 8.6
White silk	(1) 7.1	(1) 8.3
	(2) 7.1	(2) 8.2

The analyses (1) and (2) were duplicate determinations, and always showed concordance, but the two methods yield different results. For some reason a constant error is introduced, but the cause is not very obvious. A possible explanation is that amine sulphates are formed instead of ammonium sulphate, and that the amine is distilled off with ammonia in the ordinary process and neutralizes some of the standard acid, but that it is not acted upon or estimated in the formaldehyde process. Longer digestion with sulphuric acid might overcome this difficulty.

The author's thanks are due to Mr. Arnold Seymour Jones for his assistance in carrying out the experimental work recorded above.

THE COMMERCIAL CONTROL OF TANNERY LIME LIQUORS.[1]

By Hugh Garner Bennett, M. Sc.

The lime liquors used for the depilation of hides and skins in leather manufacture are always used for several packs of goods, and although a new lime liquor is an almost completely sterile medium, the solvent effect it exerts on the various proteid matters which enter it causes a gradual increase in the amount of organic matter which is in solution. In this way it is made possible for certain bacteria to thrive, and these also assist in dissolving further quantities of both keratinous and gelatinous matter. When such liquors therefore are repeatedly used, there is not only a rapid accumulation of hydrolytic and putrefactive decomposition products of the proteids, but also an almost proportionate multiplication of the fermentive organisms; and it is evident that if this repeated use be continued indefinitely, the liquor will continue to unhair, but by virtue of its bacterial rather than its chemical activity.

In the manufacture of many leathers it is important that this bacterial action should not be taken too far, and it is in all cases desirable to know how far it is necessary, and to ascertain whether any given lime liquor is likely to produce the desired effect. Many processes have therefore been suggested for determining the age and degree of "mellowness" of an old lime liquor. The

[1] From the *J. S. C. I.*

most obvious way is to determine the amount of dissolved hide substance in the liquor by the estimation of nitrogen by Kjeldahl's method, but this is far too tedious for the control of the ordinary lime yard, and is resorted to only in special cases. The estimation of the free ammonia has also been taken to indicate the age and character of such lime liquors, partly under the impression that this ammonia had a powerful unhairing action, and partly with the idea that its quantity was at any rate roughly proportional to the total dissolved hide-substance and also to the bacterial activity. The accurate estimation of ammonia in lime liquor, however, is a matter of some difficulty, and usually involves a somewhat complicated apparatus. It has recently been stated, moreover, that ammonia in old limes does not give the depilatory and solvent effects so long attributed to it, and that the effect of old limes is due almost entirely to bacterial action. The estimation of peptone acids formed by the action of formaldehyde after the removal of the lime with zinc sulphate, has recently been proposed as a measure of the dissolved hide-substance, but its author, as well as the present writer, found that the results it yields are by no means strictly proportionate to the nitrogen determined by Kjeldahl's method.

The method now suggested has been employed by the author for some years, but because of its somewhat empirical nature and scientific imperfections, he has not thought it desirable to publish it. The present paper is due to the fact that it was found to be more accurate than was expected, and also because it was found to be exceedingly useful and convenient for control work. The decomposition of the proteid matters of the skin results in formation of peptones, the calcium salts of amido acids and other weak acids, amines and a certain quantity of ammonia, all of which are of a weakly basic nature. The method of determining these is simply to titrate 25 c.c. of the filtered lime liquor with N/10 hydrochloric acid in the presence of phenolphthalein and methyl orange, the former being sensitive only to the strong bases (*e. g.*, lime), whilst the latter is also sensitive to the weak bases mentioned above. The 25 c.c. liquor are placed in a white porcelain basin and diluted somewhat with distilled water. Phenolphthalein (3 drops of a 1 per cent. solution) is added, and the N/10 acid slowly run in with constant

stirring until the pink color just disappears; the volume of acid used being then noted. Methyl orange (2 drops of a 0.1 per cent. solution) is now added to the basin, and the addition of standard acid continued until the indicator first distinctly changes towards red; the volume of acid used is again noted. The difference between the two readings represents the weak bases formed by the decomposition of the hide, and is proportional to the "dissolved hide-substance" and to the bacterial activity and "mellowness" of the lime liquor. It is of course known that the end-point in titrating ammonia in the presence of phenolphthalein is not very accurate, but the quantity of ammonia in ordinary lime liquors is usually small, and forms a very meagre proportion of the nitrogenous decomposition products, and hence the error caused by its presence is not sufficient to impair seriously the accuracy of the method. The end-point with methyl orange, on the other hand, is not perfectly sharp, but can usually be confirmed very closely by a duplicate titration. The following results were obtained with a series of lime liquors, using the above method, and also estimating nitrogen by Kjeldahl's method and by the formaldehyde method recently suggested by the author.

(1) Titration difference for 25 cc. lime liquor using N/10 hydrochloric acid	(2) Ammonia obtained by Kjeldahl method; equivalent in N/10 sodium hydroxide	(3) Formaldehyde method, No. of cc. N/10 sodium hydroxide required	Ratio of column (3) to column (1)
4.10	2.80	2.80	0.68
5.37	3.50	3.55	0.68
11.0	7.45	7.50	0.68
11.75	8.05	8.10	0.68
13.5	9.05	9.10	0.67

The relative concordance between the various methods with lime liquors so widely varying in age was greater than the author expected, and at any rate justifies the process now suggested for control work. The above results were obtained with lime liquors from a large leather factory where a regular system of liming is employed, and it may be taken therefore that for these liquors, 1 c.c. titration difference (with N/10 hydrochloric acid and 25 c.c. liquor) corresponds to 0.0053 grm. of dissolved hide-substance. The author has received about 30 other comparative analyses of lime liquors from the factory, all of which confirm this factor. The most discrepant results occur with the comparatively fresh limes, in which the titration difference is

small; a slight error in the end point causing a comparatively large percentage error.

It is possible, of course, that other tanyards with other systems of liming may find a different factor, but the probability is that it will be constant for any regular system. In cases where a small amount of sulphide of sodium is regularly used to assist depilation, a constant error will be introduced in the factor, depending upon the amount of sulphide. The titration must also in this case be conducted with considerable dilution; the sodium hydrate and sulphydrate formed from the sulphide being then accurately alkaline and neutral respectively to phenolphthalein, whilst both are alkaline to methyl orange. In cases of quick depilation with considerable quantities of sodium sulphide, the most useful figure will be the total alkalinity as determined with methyl orange. The author desires to thank Mr. Arnold Seymour Jones for his assistance in carrying out the analytical work here recorded.

THE DETECTION OF SULPHITE-CELLULOSE LIQUORS IN TANNING EXTRACTS.[1]

By Prof. H. R. Procter and S. Hirst.

In the manufacture of paper pulp by the bisulphite process, the coniferous woods are digested under pressure with a solution of calcium bisulphite, which dissolves the ligneous constituents, leaving a comparatively pure cellulose. Enormous quantities of the used sulphite liquors, containing large amounts of dissolved vegetable matter, are run into rivers, or into the sea. It has been found, however, that after suitable decolorization and concentration in the vacuum pan, these liquors will yield an extract very similar in appearance to oakwood and which when analyzed by the I.A.L.T.C. official hide-powder method, will show about 25 per cent. of tanning matter or substances absorbed by hide. Such a purified extract has been put upon the market under the name of "Pinewood" or "Fichtenholz" extract. If attempts are made to tan with this extract alone, it is difficult, if not impossible, to obtain a product which will deserve the name of leather, the surface being apparently tanned, while the interior

[1] From the *J. S. C. I.*

remains raw and unaltered, and the hide dries horny and usually of unsatisfactory color. If, however, the hide be in the first instance partially tanned with some ordinary tanning material, or if some other tanning extract be used in conjunction with the pinewood extract, leathers are produced similar in appearance to those of ordinary tannages, as the pinewood extract appears capable of absorption, giving firmness and weight, although it probably contains no bodies analogous to the ordinary tannins. It may therefore ultimately become a useful addition to the tanner's resources, but while experiments with it were at first apparently successful as a weighting and solidifying tan, some constituent appears to accumulate in the liquors which led ultimately to the production of brittle or tender leather. Whether this was due to mismanagement, the writers cannot at the moment say, but so far as they are aware, but little of the extract has been sold to tanners under its own name. It is, however, obviously a tempting material for the extract manufacturer, as considerable quantities can be added to tanning extracts without altering their appearance, and it shows a good percentage of tanning strength by the ordinary method of analysis. It is therefore important in the interests of the tanner that means should be discovered for the detection, and if possible, the estimation of pinewood extract in mixture, and a good deal of time has been devoted by the writers to the attempt to discover a satisfactory qualitative color reaction, and it has been found that the following modification of the ordinary test for lignine with aniline and hydrochloric acid is very delicate and quite satisfactory.

To 5 c.c. of the extract solution, which should be of about the ordinary strength employed for analysis, 0.5 c.c. of aniline is added, and the whole is well shaken, and 2 c.c. of concentrated hydrochloric acid is then added to the mixture. With all ordinary extracts this has the effect of immediately clearing the turbidity caused by the aniline, and a perfectly transparent solution results, but where pinewood extract is present, even in comparatively small quantity, a precipitate is rapidly produced which gradually rises to the top of the liquid. Heating is not necessary, and on the whole not desirable, though it sometimes increases the rapidity of the separation of precipitate. The reaction, however, is immediate, and any slight turbidity which arises after

considerable standing should be disregarded, as it sometimes occurs in the case of unmixed extracts, possibly from minute traces of ligneous matter. It is possible that this method may be developed into a quantitative form, but this has not yet been attempted by the authors.

It was also found that the "tanning substance" of the pinewood, while it was estimated as tannin by the ordinary hide-powder process, was only to a very small extent capable of reducing permanganate in the Löwenthal method, and therefore gave almost negative results in tannin, a pinewood extract showing about 25 per cent. of matters absorbed by hide being only equivalent by the Löwenthal method to about 4 per cent. of gallotannic acid. This property of low oxidizability is not shared to nearly an equivalent extent by any ordinary tanning material, and therefore pinewood extract can be detected, and even estimated approximately if present in considerable quantity, by comparison of the gravimetric and Löwenthal results.

The following table gives the values as compared to gallic acid of the tanning matters absorbed by hide-powder from 3 samples of sulphite cellulose extract, and average values for those of oakwood and chestnut extracts, with which it is most likely to be mixed.

	Extract	Gallic acid value of 1 grm. tannin
"Fichtenholz"	I	0.129
"	II	0.090
"	III	0.137
"	average	0.119
Chestnut	"	0.604
Oakwood	"	0.527

It was hoped by the authors to develop on this basis an approximate quantitative method; and arithmetically, if a be the gallic acid value of the genuine extract, b the (lower) value for "pinewood," and c that experimentally found for an unknown mixture, $\frac{a-c}{a-b}$ should be the fraction of the total "tannin" found by ordinary gravimetric analysis which is due to "pinewood." Not only, however, are the required constants usually unknown, and subject to considerable variation in the different extracts made from the same material, but even when the method is applied to known

mixtures, the results are only approximate, and usually indicate less than the actual amount of "pinewood" really present, suggesting that the absorption of one of these matters by the hide is affected by the presence of the other. This point is still under investigation, and may lead to interesting results.

THE USE OF THE LOEWENTHAL METHOD IN THE CONTROL OF TANNERY LIQUORS.[1]

By Prof. H. R. Procter and S. Hirst.

For the purposes of a recent paper on "The Detection of Sulphite Cellulose Liquors" (see page 146), factors were determined for the calculation of Löwenthal results to equivalent values of tanning matters" as estimated gravimetrically, for a considerable variety of extracts and other tanning materials. The Löwenthal method is fully described in Procter's "Leather Industries Laboratory Book," and details need not be repeated, but as a large number of titrations had to be made, some mechanical improvements were adopted which greatly facilitated the operation. Self-filling burettes of the simple form shown in the figure were used both for permanganate and indigo, and the titration was carried out in a beaker of about 1 liter capacity fitted with a spindle carrying two small screw propellers, made either of stiff celluloid or of brass coated with celluloid varnish, and driven by a small turbine or electric motor. For comparison, a similar beaker filled with an already titrated liquor was placed in a similar light and beside that in use. Under these conditions titrations were very rapidly made and with almost absolute concordance, and the systematic use of the method for control of the tanning strength of liquors naturally suggested itself. Of course there is nothing new in such an idea, but no carefully thought-out and systematic mode of work has hitherto been published. For practical purposes the method requires to be as simple and as rapid as it is compatible with concordant results, and as tanning materials are now almost universally bought by the I.A.L.T.C. method of analysis, it is important that the figures should be comparable with this method, and on this account detannization by chromed hide-powder was preferred to that by

[1] From the *J. S. C. I.*

gelatine, although the latter is theoretically more exact, being less affected by astringent non-tanning matters, such as gallic acid.

Since the actual amount of permanganate used varies somewhat with the operator and the details of titration, the usual method of calculating the results of a Löwenthal analysis is by direct comparison with a supposed pure solution of gallotannic acid, but as actually pure gallotannic acid cannot be obtained, allowances have to be made for an assumed but unascertained amount of impurity; commercial gallotannic acid of the best quality usually reducing more permanganate than the theoretically pure substance. Gallic acid, being crystallizable, is readily obtained in a pure form, and is oxidized by permanganate in a similar way to gallotannic acid, 1 grm. of crystallized gallic acid reducing approximately the same amount of permanganate as 1.34 grms. of the portion of the purest obtainable gallotannic acid absorbed by chromed hide-powder. There is, however, little advantage in calculating in this way, since few, if any, of the tanning materials in use contain solely gallotannic acid, and the different tannins are well known to reduce permanganate in somewhat varied proportions. It is therefore more practical and convenient to state the results of experiment in terms of gallic acid, and it is easy to obtain a factor by which the latter can be approximately calculated to any tannin as determined by the hide-powder method.

The following solutions are employed:—(1) Pure air-dried gallic acid, 0.1 grm. per 100 c.c. freshly made. (2) Purest indigo-carmine, 5 grms. per liter, with 50 grms. of concentrated sulphuric acid, 25 c.c. being used for each determination. A solution of 1 grm. "indigo pure B.A.S.F." in 25 c.c. concentrated sulphuric acid diluted to 1 liter with 25 cc. added sulphuric acid, may also be employed. These solutions both keep well. 25 c.c of either must require 25-30 c.c. of permanganate for oxidation, or a larger measured volume must be used. (3) Permanganate of potash solution, 0.5 grm. per liter, made by the dilution of a 5 grm. per liter solution at frequent intervals, as very weak solutions do not keep satisfactorily.

The liquor to be tested must be so diluted that 5 c.c. will not consume more than two-thirds of the permanganate required by the 25 c.c. of indigo always used, and thus the complete titration

can always be made with the contents of a 50 c.c. burette. Sufficiently accurate readings can be made from the upper edges of the liquids without the use of a float. It is important that the stirring turbine should run with fair uniformity (if hand-stirring is relied on, it must be constant and efficient), and the dropping should be at a regular rate. Generally this may be as fast as separate drops can be counted, until the original blue color has become yellow-green, after which permanganate is added drop by drop to complete discharge of the blue. It is well occasionally to time the titration so as to ensure constant work. The titration is even more easy by good artificial light diffused by ground glass or tissue paper than by daylight, the removal of the last trace of blue being shown by a very marked brightening of color; but as the end-points are not quite identical, all the titrations for any single analysis must be done in the same light.

The tanning matter is of course indicated by the *difference* of titration of the original and detannized liquor, but as neither dissolved salts or traces of hide-substance have any appreciable effect on the titration, the detannization may be much simpler than that required for actual gravimetric analysis. Washing of hide-powder after chroming is quite needless, the powder being merely chromed, pressed, weighed, and the requisite water added; and 6 c.c. of the detannized liquor counted as five; but a still greater simplification may be effected by the use of Prof. Paessler's dry "lightly chromed" powder, or by the use of freshly air-dried chrome leather machine shavings as suggested by Kopecky. About 7 grms. of the dry powder and a little kaolin should be added to 100 c.c. of the diluted liquor, well mixed by hand shaking, and shaken for 10-15 minutes in the machine. The moisture of such a quantity of powder only amounts at most to 1 grm. even if the whole of it acts as water of dilution, which is very doubtful, and can at most cause an error of 1/100th of the total tannin in the diluted liquor; and as the analysis is only for comparative purposes, and the error, such as it is, is a constant one, it may well be neglected. The detannized liquor is filtered till clear through paper, and 5 c.c. is with 25 c.c. of indigo twice titrated. If the work is systematic, the amount of dilution required for each class of liquor will be known sufficiently nearly; if not, a simple titration of the undetannized

liquor will be a sufficient guide, and for this purpose it is better to dilute too much than too little. The final result is of course divided by the number of c.c. of original liquor taken per liter and multiplied by 1000. It is best to use distilled water for this dilution, but any good tap water will do for titration. Whether the liquor should be filtered clear before or after dilution, or not at all, is a matter for consideration; but if not, any suspended reds, such as those of quebracho, or the catechin of gambier, will largely dissolve on dilution, and be estimated as tannin, which is not necessarily an error, since to some extent the same thing happens as liquors become exhausted in the tannery. It is not necessary to filter the liquor for detannization, and a good compromise would be to filter only the portion of diluted liquor required for titration, through any good quantitative paper. The systematic method of work would then be that the liquors to be tested would be brought to the laboratory first thing in the morning, and there diluted as required. 100 c.c. of each of the diluted liquors would be placed in shaking bottles with the requisite dry chromed hide-powder and kaolin and shaken by hand till well mixed; and a portion of each of the diluted liquors filtered, the first turbid portions being rejected. The operator would then shake the bottles in the machine, and set their contents to filter while he proceeded with the titrations of the diluted liquors.

The first step is to make fresh the weak permanganate by diluting 100 c.c. of 5 grm. per liter strength to 1 liter as the strong solution keeps well while the weak soon alters, and to shake this very thoroughly in the stock-bottle to ensure complete mixture. 25 c.c. of the indigo is then twice titrated alone, and the titration repeated with 5 c.c. of the freshly-made gallic acid solution, 0.1 grm. in 100 c.c. The sum of the differences between these will give the permanganate value of 0.01 grm. of gallic acid, which will be practically constant from day to day with careful work and a single operator, and perhaps need not be every day repeated.

The titration of 5 c.c. of the diluted liquors is now similarly performed, and then that of 5 c.c. of the corresponding detannized portions, the titrations always being done in duplicate to check possible errors, and the sum of the two results taken. If now

TABLE I.

Material	Tannin value of 1 grm. gallic acid	Gallic acid value 1 grm. tannin	Gallic acid value 1 grm. non-tans.
Chestnut extract	1.52	0.655	0.095
" "	1.67	0.596	0.085
" "	1.64	0.607	0.080
" "	1.77	0.565	0.199
" "	1.70	0.590	0.200
Solid chestnut extract	1.66	0.600	0.245
Chestnut wood	1.61	0.618	0.313
Average	1.65	0.604	
Oakwood extract	1.79	0.557	0.115
" "	1.93	0.516	0.047
" "	1.98	0.504	0.068
Oakwood	1.88	0.531	0.116
Average	1.89	0.527	
Myrabolams extract	1.70	0.586	0.157
" "	1.82	0.549	0.185
Myrabolams	1.67	0.597	0.126
Average	1.73	0.577	
Mimosa D. extract	1.74	0.574	0.053
" "	1.66	0.602	0.184
" "	1.71	0.584	0.094
Liquid quebracho extract	1.63	0.612	0.222
Quebracho wood	1.70	0.588	0.220
Average	1.69	0.592	
Larch bark	1.96	0.509	0.056
Hemlock bark	1.97	0.501	0.083
Hemlock extract	2.28	0.437	0.035
Spruce bark	2.53	0.395	0.104
Average	2.18	0.460	
Valonia extract	1.80	0.553	0.060
Valonia	1.58	0.632	0.086
Sumach	1.53	0.650	0.073
"	1.47	0.680	0.084
Oakbark	1.71	0.583	0.112
Mimosa bark	1.88	0.529	0.031
Mangrove bark	1.46	0.682	0.004
Gambier cube	1.78	0.559	0.325
Average of all above materials	1.76	0.573	
Gallotannic acid	1.34	0.742	....
Fichtenholz I ("Pinewood extract")	7.75	0.129	0.096
Fichtenholz II	11.11	0.090	0.043
" III	7.3	0.137	0.031
Average	8.72	0.119	

the result of the detannized liquor be deducted from that of the original diluted liquor the quantities of permanganate consumed by indigo will cancel each other, and the result will be the permanganate value of the tannin of 10 c.c. of (diluted) liquor; and

Permanganate consumed by gallic acid	:	permanganate consumed by liquor	::	1 grm. per liter gallic acid	:	grm. per liter of tannin in liquor expressed as gallic acid.

If for 1 grm. per liter, the weight of the actual tannin corresponding to 1 grm. of gallic acid be substituted, the strength of the diluted liquor will be obtained directly in grm. per liter in "tanning matter;" and from this by simple multiplication by the dilution, that of the original liquor. 1.34 in place of 1 will give the strength in terms of gallotannic acid; 1.76 is the average of about 30 analyses of all the common tanning materials, and Table I. gives factors averaged from several analyses of each of the more important.

If, however, it be desired to obtain an actual experimental figure for the liquors of the particular tannery, or for any particular tanning material, this is easily done by combining the Löwenthal with an ordinary gravimetric analysis of an average liquor by the shake method; the actual "total soluble" and "non-tannin" solutions being used for the titration. Then the result in grm. per liter found gravimetrically, divided by the "gallic acid value" by Löwenthal, will give the factor required, *viz.*, the weight of the tannin corresponding to 1 grm. of gallic acid.

The Löwenthal method as applied to liquors not only has the advantage over the gravimetric method of much greater rapidity, but is probably of greater relative accuracy with weak liquors, as no concentration is required; the following figures obtained independently for a set of liquors by two different students illustrating the sort of concordance to be expected. The factor used was 10/16 or 1.66, which was the average of several determinations of the materials used.

The method is one which can easily be mastered by any intelligent youth without much chemical knowledge, and if it were combined at the same time with lime-water determinations of acidity, would give information as to variations in the working of a yard which could hardly fail to be valuable commercially. It is, however, only to be recommended for continuous and system-

TABLE II.

Liquor	Tanning matter per cent. A	B
1st Suspender	0.17	0.17
2nd "	0.39	0.39
1st Handler	0.85	0.82
2nd "	1.20	1.20
3rd "	1.48	1.50
4th "	2.13	2.12
5th "	3.33	3.27
6th "	4.23	4.21

atic work, and its use for occasional analyses is more troublesome than the ordinary gravimetric method.

The method is equally adapted to the control of spent tans, since very weak liquors can be as accurately determined as strong ones, 10 c.c., or more, if necessary, being used for each titration instead of 5, so that a sufficient quantity of water can be used for complete exhaustion. The material can be dried, ground fine, and extracted in the Procter extractor in the usual way; but for comparative tests it would often be sufficient to boil up 5 lbs. of the wet material, as it comes from the leaches with a gallon of water for half an hour, allow to stand overnight, and draw off the liquor, making up to one gallon, if necessary, by the addition of enough water to the material to supply the loss by evaporation, and Löwenthal the liquor. Though this would give no precise information as to the exact amount of tannin left in the material, it would at once detect any variations in the completeness of the leaching, and if compared to an occasional more complete analysis, would probably give all necessary information.

As regards the theoretical significance of the Löwenthal results, it is interesting to note that the table of factors given, partially bears out the statement formerly made that catechol tannins reduce materially less permanganate than gallotannic acid or pyrogallol tans. 1 grm. of the purest gallotannic acid is only equal in reducing power to 0.742 grm. of gallic acid, and in all cases the reducing power of the "tanning matters" absorbed by hide-powder is still lower, the highest being that of sumach, of which in one sample 1 grm. had equal reducing power to 0.680 grm. gallic acid; while the lowest are the tannins of coniferous barks, ranging from about 0.4 for spruce bark to 0.5 for larch

and hemlock. Chestnut extracts average about 0.6. Oakwoods and myrobolams range from 0.5 to 0.6, while mangrove bark, a pronounced catechol tan, reached 0.68. These differences are not so large as was *a priori* to be expected, a fact which greatly facilitates the use of the method for liquor testing, but which proves that the permanganate required is dependent rather on the differences of constitution of the individual tannins than on the catechol or pyrogallol nucleus. It is also evident that even in those tannins most allied to gallotannic acid, the substance estimated by hide-powder is not simply gallotannic acid, but either includes other less oxidizable matters or compound tannins of a more complex character, and very possibly in many cases, glucosides.

The gallic acid values of the different tannins are characteristics which may be used, like the saponification values and iodine values of fats, as a means of identification. Thus an "oak-wood" extract with a gallic acid value over 0.6 may be justly suspected of being a chestnut. Even in genuine extracts the differences in value which are found, no doubt point to real differences in the character of the tannin due to manufacture, mode of growth, or age, which deserve closer investigation.

In this connection it may be interesting to quote some results of detannization by gelatine (described in Procter's "Leather Industries Laboratory Book"[1]), as compared with various hide-powders. It has been shown that by this modification of the method, the separation of gallotannic acid from gallic acid is very approximately accurate, although perhaps by a compensation of errors, traces of gallic acid being precipitated and traces of the tanno-gelatine dissolved in the acid liquor. Addition of more salt diminishes the latter error, but increases the former.

TABLE III.—GALLIC ACID EQUIVALENT TO NON-TANNINS.

Extract	Gelatine salt and acid	Freiberg unchromed powder	Vienna unchromed powder	Paessler chromed powder	American chromed I. A. L. T. C.
Oakwood, (reputed)..	0.255	0.221	0.163	0.149	0.149
Oakwood, Gondolo...	0.160	0.144	0.132	0.115	0.115
Chestnut, solid.....	0.331	0.354	0.320	0.242	0.245
Chestnut, liquid	0.297	0.300	0.297	0.209	0.199

It will be observed that in most cases the non-tannins are

[1] To 50 c.c. of liquor add 25 c.c. of fresh 2 per cent. gelatine solution, 25 c.c. of a saturated solution of salt containing 50 c.c. of sulphuric acid per liter, and a teaspoonful of kaolin, shake for 15 minutes and filter and titrate 10 c.c. instead of 5 c.c.

highest in the case of gelatine precipitation, though in some cases they are approached or even exceeded by the unchromed hide-powders used by shaking, while those of the chromed powders are invariably much lower. It appears therefore that as regards the oxidizable matters estimated by permanganate, the unchromed powders give results nearer the scientific truth, but the much closer concordance of the chromed powders fully justifies their use for commercial purposes, and further it must be remembered that in gravimetric analysis these oxidizable and generally astringent non-tannins form only a small portion of the whole. The close agreement of Prof. Paessler's lightly chromed powder with that officially chromed, establishes the suitability of the former as a detannizing agent for the Löwenthal process, and encourages the hope that a dry chromed powder may ultimately be produced, which will avoid not only the chroming, but the much more troublesome washing immediately before use which is now required.

If the gelatine method is preferred to hide-powder for liquor control it is quite as rapid, and probably less affected by large amounts of non-tannins, but the results are not directly comparable with gravimetric analysis, and some samples of gelatine exercise a slight reducing effect on permanganate, not amounting in blank experiments to more than about 0.2 c.c. per 10 c.c. of the non-tannin filtrate, and probably due to traces of sulphites. This, if desired, is easily determined and allowed for.

NOTE ON THE DIFFUSION OF CHROMIUM, IRON AND ALUMINIUM SALTS THROUGH GELATINE JELLY.[1]

By Prof. H. R. Procter and Douglas J. Law.

The experiments described in the following note were prepared in the first instance as a lecture demonstration, but though the results throughout must merely be regarded as qualitative they appear to present some points of interest which make them worthy of a permanent record.

If a solution of a colored crystalline salt, such as copper sulphate, is poured on the top of solidified gelatine jelly, it diffuses into it somewhat rapidly, its progress being easily traced by the

[1] From the *J. S. C. I.*

change of color in the transparent jelly. It has been shown by Fick that in many cases diffusion in jellies is practically as rapid as in still water. In the case of colored substances of a less definitely crystalline character the diffusion is slower, and the ultimate penetration less, while solutions of a distinctly colloidal nature either do not penetrate at all or do so to a comparatively small extent. If a mixture of two colored substances is employed of different degrees of diffusibility two zones of diffusion are formed, of which the deeper consists only of the more diffusible substance. When operating with colorless salts, bases, or acids, it is frequently easy to determine their progress by the addition of a suitable indicator, thus that of strong bases is shown by the addition of phenolphthalein, or that of acids, by the same reagent colored with a trace of caustic alkali.

As salts of chromium and other metals of the same group are very prone to hydrolysis and the formation of basic salts, it was of interest to determine not merely the progress of the chrome salt but that of the hydrolyzed acid, and for this purpose a 5 per cent. jelly was used colored pink with slightly alkaline phenolphthalein. This was allowed to set in Nessler cylinders, or for the purpose of lantern demonstration, in parallel-sided cells, and the solution to be tested was poured upon the top of the jelly. That gravitation had little influence on the rapidity of the diffusion was proved by repeating a similar experiment with an inverted tube. As the chrome salts diffused into the jelly, their progress was clearly noted by their color, which, whatever the color of the solution, is generally in the jelly of a dull bluish green, somewhat between the color of the well-known green and violet modifications. As, however, the chrome salts hydrolyze considerably, the penetration of the acid was much more rapid, with the consequence that a broad zone was formed beyond the chrome in which the color of the phenolphthalein was discharged. As a rule the boundaries of these zones, though naturally shading into each other, were sufficiently sharp to allow of easy approximate measurement, especially as regards the edge of the diffused chrome salts. That of acid was distinctly sharper in the case of chrome alum than in that of chromium chloride solution. The results of these experiments are shown in the following tables, the depth of diffusion being stated in centimeters.

Experiments were made with a half-saturated solution of chrome alum containing about 1 per cent. of chromium and with a 10 per cent. solution of chromium chloride containing 1.4 per cent., 10 c.c. being in each case placed above the gelatine in the Nessler tube. As the first experiments were not intended to be qualitative, this solution was not renewed, but it must be observed that under these conditions the diffusing solution must become continuously weakened with the progress of the diffusion, so that in the later stages the diffusion would go on very slowly. Before any calculations therefore could be made, this would have to be taken into account, together with the possible swelling or contraction of the jelly, and if it were possible to apply the method quantitatively it would probably be better to employ larger quantities of the solution kept gently stirred and replaced by new solution before sensible change had taken place in the concentration. Both solutions of the normal salts and others rendered basic with definite additions of sodium carbonate were employed, and one of the most striking facts observed was that the rate of diffusion and the apparent amount of hydrolyzed acid was in the case of chrome chloride unaffected by these conditions, and the differences scarcely if at all exceeded that of probable experimental errors, while with the chrome alum, the diffusion of the chromium was rendered much slower, but without any corresponding influence on that of the acid. From a solution of chrome alum rendered green by boiling, the diffusion of acid was much more marked than from the violet normal salt, supporting the view that the change of color was due to hydrolysis and the formation of a basic salt. As has been noted, the solution of chromium chloride employed was materially stronger than that of the chrome alum, and perhaps this may explain the differences of effect. A further experiment is in progress with solutions of equal chromium concentration.

The rate of diffusion was found to be quite independent of the bore of the tube.

An interesting effect noticed in some of the experiments both with chromium chloride and chrome alum was the production of strioe or layers of green parallel to the surface and of greater intensity than the layers above and below. These recall the somewhat similar effects observed in the diffusion of bichromate

in gelatine containing traces of silver nitrate, or conversely of silver nitrate in bichromated gelatine. The latter has been recently investigated by R. E. Liesegang (Kolloide Z., 1907, 2, 70), who finds that it is much influenced by the presence of gelatoses or decomposed gelatine. Ostwald has explained the phenomenon as due to the existence of a supersaturated solution of silver chromate which diffuses without precipitation to a certain concentration at which "germs" are spontaneously formed, and the concentration falls to saturation, and again diffuses till it again becomes sufficiently supersaturated. Liesegang points out that the gelatoses increase the solubility of silver chromate. Although no two salts which mutually give rise to a less soluble one are present in the green chrome solutions, the explanation is probably somewhat similar. The hydrolytic dissociation and diffusion of the acid makes the salt continually more basic until at last a part becomes incapable of further diffusion, and possibly acts as a semipermeable membrane to the more basic part, while the more acid or normal portion diffuses further until it in turn becomes too basic. It is also possible that the basic salt passes spontaneously from the sol to the gel condition at a certain degree of basicity, leaving a more acid salt in solution, as it is well known that when separation takes place in such basic solutions, the portion unprecipitated is much more acid than before, the gel formation being only reversible in presence of considerable excess of acid.

The phenomena in the case of iron and aluminium salts are very similar in character to those just described, the diffusion of the acid always considerably preceding that of the base. In the case of ferric chloride, the salt fixed is of the deep brown characteristic of basic ferric salts. With alumina it is of course colorless, but may be made visible by the addition of a trace of yellow logwood infusion with which alumina forms a violet lake.

The experiments described are not only interesting as demonstrating in a striking way the hydrolysis of such salts, but also illustrate what has long been taught by one of us, and has recently been fully proved by Stiasny (Collegium, 1908, 337; this J., 1908, 1030), that the acid and the colloidal base are absorbed independently by the amphoteric gelatine or gelatigenous hide-fiber, and that either may be absorbed in excess according to the conditions of the experiment.

Diffusion of Chrome Chloride in Gelatine.

Basicity of chromium chloride solution. 10 c.c. 10 per cent. $CrCl_3 6OH_2$.	19 hours		67 hours		91 hours		115 hours		139 hours		163 hours		17 days	
	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid
About 1.4 per cent. chromium														
Normal salt	1.8	2.1	3.1	3.5	3.6	4.0	4.2	4.6	4.6	5.0	5.0	5.4	7.6	..
+1.3 c.c. N/1 Na_2CO_3	1.7	2.0	3.1	3.4	3.6	4.0	4.2	4.6	4.6	5.0	5.0	5.4	7.6	..
+2.6 c.c. N/1 Na_2CO_3	1.7	2.0	3.1	3.4	3.6	4.0	4.1	4.4	4.5	4.9	4.9	5.3	7.6	..
+5.7 c.c. N/1 Na_2CO_3	1.7	1.9	3.1	3.5	3.6	4.0	4.1	4.5	4.5	5.0	4.9	5.4	7.3	..
As basic as possible	1.6	2.1	3.0	3.6	3.5	4.1	4.1	4.7	4.5	5.1	4.9	5.5	..	..

Diffusion of Chrome Alum in Gelatine.

Basicity of chrome alum solution. About 1 per cent. chromium ½ saturated chrome alum (about 5 per cent.)	19 hours		67 hours		91 hours		115 hours		139 hours		163 hours		17 days	
	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid	Chrome	Acid
Normal salt	1.1	1.2	1.9	2.1	2.2	2.5	2.6	3.0	2.9	3.3	3.1	3.5	4.7	5.3
+1 c.c. N/1 sodium carbonate	0.9	1.5	1.6	2.2	2.2	2.6	2.3	2.9	2.5	3.1	2.7	3.4	4.1	5.0
+2 c.c. N/1 sodium carbonate	0.8	1.9	1.3	2.4	1.7	2.8	1.9	3.1	2.0	3.4	2.1	3.6	3.0	4.9
As basic as possible	0.7	1.7	1.2	2.3	1.6	2.7	1.7	3.5	1.8	3.3	1.9	3.4	2.5	4.7

ABSTRACTS.

The Sugars of Oakwood Extracts. JAN JEDLIKA. *Collegium*, 1909, Nos. 351-2, pp. 113-126. The previous literature on this subject is limited to the work of Schröder and his associates on the determination of mono-saccharides with Fehling's solution. (*Dingl. Polyt. Journ.* [293] 229). Böttinger (*Liebig's Annalen*, [259] 132) attempted to isolate osazones without characterizing them. The author's investigations were carried out on the Mitrovitz oakwood extract of 14-15 per cent. non-tans.

1. *Non-hydrolyzed Non-tans.*—The tans and dye-stuffs were first precipitated according to Schröder's method with basic lead acetate. The excess of lead was removed by adding sodium carbonate which imparts to the colorless solution a yellow color when in excess, easily observed in a porcelain dish. Any excess of soda may be neutralized with acetic acid, although a slight alkalinity does not affect the result. The sugar precipitation by Fehling's solution was made precisely according to Allihn. The cuprous oxide was allowed to settle, washed by decantation, filtered off and finally weighed as CuO (according to Prager). Ruhsam's tables for calculation of glucose, 30 min. boiling, were used. During another investigation on the preparation of the pure tan-stuffs of oakwood, it was found that the fractional precipitation with lead salts carried down non-tans with the tans, especially in the last fractions. It was thought therefore that in these experiments an extract after precipitation with lead subacetate would contain less sugar than when the detannization had been effected with hide powder. This however was not the case. The hide powder non-tans in most cases contained 0.2 to 0.3% less sugar, showing that mono-saccharides are partially held back by the hide, which many have disputed. Forty analyses made in the course of eight years showed 3.2% sugars in the non-hydrolyzed non-tans. Schröder found an average of 3.07% sugars in Slavonic extracts of 59.8% water.

2. *Hydrolyzed Non-tans.*—Sulphuric acid was used for the hydrolysis, on account of its easier removal, although hydrochloric acid reacts twice as rapidly. Solutions freed from tans both by hide and lead were used. The H_2SO_4 was added to 2% contents and the whole heated 4 hours on the water-bath with inverted condenser. After cooling, the acid was fixed with lead carbonate and filtered off. Some lead went into solution, and was removed by soda. In the hydrolysis it was found that increasing the time of boiling did not much increase the amount of sugar and some furfural was formed. One lead subacetate non-tan gave:

With	4	hours	boiling	and	2	per cent.	H_2SO_4,	.0811	gm.	glucose
"	2	"	"	"	1	"	"	.0718	"	"
"	2	"	"	"	2	"	"	.0770	"	"
"	6	"	"	"	2	"	"	.0823	"	"

In all sugar determinations an amount of solution was taken giving approximately the same amount of CuO (0.18 to 0.22 gms.) The hide powder product was not found to contain more reducing substance than that from the lead precipitation, although lead acetate certainly precipi-

tates gum-like substances which yield mono-saccharides on treatment with acids. The results were variable, the extremes being 7.4 to 6.1%. The average was 7% glucose in extracts of 60% water. (The sugars actually present are not glucose, but rated as such) On the whole, when there was less sugar in the non-hydrolyzed solution, more was obtained in the hydrolyzed stage. For example, one extract of 2% sugar, after hydrolysis of non-tans, gave 7.3%, leaving 4.8% due to hydrolysis; another of 3.6% original sugar, yielded 6.8%, or 3.2% due to hydrolysis. Probably the polysaccharides are partly hydrolyzed in varying amounts during the extraction. This agrees with Schröder's results, who found in Mitrovitz oakwood of 13% water, from 4 to 7.5 parts sugar to 100 of tans, but in the extract 13 parts of sugar to 100 of tans.

3. *Hydrolyzed Extract.*—A 4-5% extract solution was hydrolyzed as before with H_2SO_4 and the tans and acid removed with lead carbonate. Higher numbers for sugar were obtained than by hydrolysis of the same extract after detannization, the average being 9.2% glucose. This is attributed to the precipitation by lead subacetate of sugar-yielding gums. It is also possible that hide absorbs some tans of the glucoside class.

Preparation of Non-tans in Large Amounts.—The hide powder separation is not suited because of the great dilution, considerable amounts of substance remaining in solution which give the iron reaction. Lead subacetate precipitation, involving following removal of lead, introduces too much mineral salts. The best process was found in the removal of the tans by rubbing with lead oxide in small portions; the yellow oxide produced by igniting precipitated lead carbonate, was found most efficient, 200 gms. being required for 1 kilo extract of 25°B. (diluted with 4 vols. water). To remove from the yellow solution the dye-stuffs which still react with iron, Schröder's subacetate solution is added until the blue coloration with ferric alum no longer appears. The solution is filtered repeatedly until clear (a Pukall porous cell being sometimes needed) and the lead which has gone into solution precipitated with H_2S. The filtrate is concentrated on the water-bath in a current of SO_2 to a syrup. For further purification this is boiled with 96% (by vol.) alcohol which dissolves the mono-saccharides. The polysaccharides separate as a slimy mass which is repeatedly extracted as long as mono-saccharides go into solution. The alcoholic extracts are concentrated to a syrup and purified by extraction with alcohol, best in a Soxhlet apparatus using quartz sand. The product will still contain some polysaccharides and mineral matter.

Hydrolyzed sugar solutions are obtained direct from the extract, boiling 10 hours over direct fire with 3 to 4% H_2SO_4; 1 kilo extract diluted to 4 litres, is used. The greater part of the acid is removed with lead carbonate, finishing with the oxide to remove tans. The remaining process is as above.

Fermentation.—Hexoses are capable of direct fermentation with yeast. The author made quantitative experiments in this direction, allowing the substance examined to ferment with fresh yeast, and weighing the evolved

CO_2. In this way the non-hydrolyzed non-tans gave CO_2 corresponding to 3.5 to 5.3% glucose (mono-saccharides) reckoned on dried substance.

Nature of the Sugars.—Galactose was tested for by oxidation of the non-tans with HNO_3, forming the difficult soluble mucic acid. This was identified by distillation of the ammonium salt, yielding pyrrol, characterized by its odor and color test. A quantitative determination of the mucic acid present was made by "inoculating" the syrupy oxidation product from 2.102 gms. non-tans with 0.1 gm. pure mucic acid; a total product of 0.17 gms. was obtained and on this basis, 4.35% galactose is reckoned (0.65% of original extract). The hydrolyzed non-tans gave slightly more.

Phenylosazones were prepared according to the standard method; 1 part reducing sugar (determined by Fehling's sol.) with 2 parts phenylhydrazine hydrochloride, 3 parts cryst. sodium acetate, 20 parts water, all boiled 1 hour in water-bath and let cool therein. The osazones from the hydrolyzed non-tans were made after first removing the mono-saccharides from the non-hydrolyzed non-tans with 96% alcohol and then hydrolyzing the product. The phenylosazone obtained from this, after crystallization from acetone melted at 153 to 155° indicating arabinose or xylose. The specific rotation was + 25° (xylose − + 19°, arabinose — + 105°) showing the substance to be xylose containing perhaps a little arabinose.

According to Tollens, the pentoses and pentosanes on boiling with HCl, split off furfural quantitatively. This is usually determined by condensation with phloroglucinol and weighing the product formed. Applying this standard method, the author found from 28.5 to 35.5% pentosanes in the dry non-hydrolyzed non-tans, or 4.3 to 5% in the original extract. Somewhat more furfural was obtained by distilling the extract direct with HCl.

Optical Rotating Power of Tannin. M. NIERENSTEIN. *Chem.-Zeitung*, [33] 126.—According to Feist, the optical activity of tannin is due to accompanying glucosides. The author attributes it however to an asymmetric C-atom in the tannin molecule, having experimentally proved that glucose free from tannin is active. The purest tannin of Schering was used, having a rotary power of 63°. A fresh solution showed the absence of gallic acid by the KCN test. A 5% solution, after detannizing with casein showed no sugar in the filtrate. A tannin solution preserved for 2 months was tested from time to time for glucose but gave no reaction. Gallic acid was found in 5 days and increased with time. On boiling the tannin solution for 2 hours with $^1/_{10}$ N.KOH, neutralizing with acid, extracting with ether and detannizing with casein, no glucose could be found.

Carbon Tetrachloride as Solvent in Fat Analysis. O. RAMMSTEDT. *Chem.-Zeitung*, [33] 93.—This solvent is not to be recommended in quantitative analysis of fats. The values are higher than those with ether which are already in excess of the truth. Moreover the last traces of this solvent are difficult to expel from the fat.

Are Cold and Hot Extracted Tans Absorbed by Hide at the Same Rate? W. APPELIUS and F. MERKEL.—*Ledertechn. Rundsch.*, 1909, No. 9, pp. 65-8.—

For these experiments, 600-1000 gms. of tanning material were first treated with about 5 litres of water at 20°C, let stand 24 hours, the liquor drawn off, residue pressed out and total liquor made up to 4 litres. The residual material was then washed with water of 20° until the washings gave but a faint iron reaction; it was then treated with 4 litres of water at 60 on the water-bath for 2 hours and the liquor obtained likewise made up to 4 litres. The residue was washed with water of 60°, and then digested with water at 90° for 2 hours, and the liquor made up to 4 litres. The following materials were thus extracted:

	Tans. per cent.	Extract I. Gms. per litre Tans	Extract I. Non-tans	Extract II. Gms. Tans	Extract II. per litre Non-tans	Extract III. Gms. Tans	Extract III. per litre Non-tans
Oak bark.....	8.8	8.58	7.12	2.33	0.69	1.30	0.89
Pine bark	10.8	6.06	8.69	4.46	2.51	1.84	0.92
Maletto bark ..	37.8	46.64	15.52	5.42	0.94	2.05	0.55
Mangrove bark	38.5	30.94	13.56	8.13	0.92	4.11	0.77
Mimosa bark ..	34.4	30.88	12.43	8.02	0.96	3.21	0.56
Myrabolams...	33.9	35.76	22.20	....	....	....	....
Quebracho wood	17.9	7.62	1.27	3.94	0.49	3.23	0.47
Valonea	28.6	18.20	14.44	13.28	3.63	....	....

Preliminary experiments in tanning duplicate samples of cow hide butt gave discrepant results, due probably to variations in surface. The tanning experiments were then made for uniformity, upon unchromed, pure hide powder (Freiberg). Liquors were prepared from the above extracts containing approximately 3 gms. in 2 litres. 20 gms. hide powder were taken to each liquor, treated 1 hour, and the residual liquors rapidly filtered and analyzed. The following table shows the percentage of tans absorbed:

	Extract I	Extract II	Extract III
Oak bark.....	85.4	88.0	73.8
Pine bark	77.4	88.9	99.7
Maletto bark	82.9	84.9	78.5
Mangrove	94.5	93.6	73.6
Mimosa bark	99.4	100.0	98.7
Myrabolams.....	80.0	....	....
Quebracho wood.....	100 0	100.0	99.9
Valonea	86.4	87.3	....

The first table shows that the non-tans are principally found in the first extract; it would seem that their presence causes the slower absorption of tans in the first fraction as compared with the second. The absorption rate is less in the third fraction and is probably due to the hydrolysis of tan-stuffs at the high temperature of extraction, producing increased non-tans as shown in the first table.

The Role of Microbes in Putrefaction of Hides. M. G. ABT (Ante, p. 86), reprint, *LaHalle aux Cuirs*, 1909, Nos. 9, 11, 12, 13; pp. 137, 173, 189, 204. *Soaking.*—This is where putrefaction is mainly produced and to be feared, even with sound hides. The contaminations with sweat, blood, etc., by

the action of water yield a medium favorable to the growth of bacteria. The water, therefore, during the first stages of soaking, should be often renewed. It is of advantage to begin with a rapid washing in the wheel or drum. Separate vats are advisable for the first and second soaking and these should be carefully washed after each lot of hides and brushed weekly with an antiseptic solution. One can judge the progress of the soaking to some extent, by analytical control, the amount of nitrogenous matter dissolved being proportional to the bacterial action. A rough estimate may be made by precipitating the albumen on saturation with salt and addition of acetic acid. Most of the fermentation products however are present as soluble amines and Kopecky has shown that these may be titrated with acid in presence of orange. Figures may be thus obtained in the factory corresponding to normal practice and useful for control. It is with salted or dried hides requiring long soaking, that putrefaction is most to be feared. The greater part of the salt may be removed by rapid washing in the wheel or drum. It is difficult to soften dried hides without damage, unless auxiliary chemicals be employed. Soda, 1 part in 1,000, sulphide of soda, 1.5 to 3 parts in 1,000 are used, 4 days being sufficient.

If the crude hides are already damaged, the suspicious indications being looseness of hair in spots, a moist and slippery feel of the hide, or evolution of ammonia, it is necessary to shorten the soaking as much as possible. Antiseptics, such as phenol, have been recommended. This doubtless arrests the fermentation, but may it not hinder depilation? Phenols are difficult to remove from hide and are more properly used to protect it during tanning. Procter advises putting the defective hides directly in weak limes without soaking.

Bating.—The bates here considered are those of bran, fowl-dung and dog-dung.

The lime left from depilation is more or less fixed by the hide and imperfectly removed by washing. Bran bates, containing fermentation acids, are active in removing lime. The author has found in such a bate after using, 0.1% free acetic acid and 0.7% combined with lime; this was weaker than a normal bate. Bates of dung dissolve lime also; amino acids formed by the fermentation of the dung in advance or of the hide during the operation, combine with the lime. The compound formed is neutral to phenolphthalein but alkaline to orange. Analysis shows that the lime is not entirely neutralized and in fact these bates frequently leave some lime in the hide. In some cases this is harmless, but in leathers which are to have a good color and are to be tanned in liquors containing little acid, it is necessary to follow the dung bate with a bran bate, in order to remove the lime. Lactic and formic acids are also used. While removing the lime, the bate also causes the hide to fall down. This shrinkage is sometimes confused with that produced by dissolving hide; both render the hide supple, but the effect produced by bates is peculiar to them. The phenomenon is of a physico-chemical nature, being studied by Procter. Hide absorbs of pure water, 6 to 8 times its weight, but in acid or feeble acid

solution, 40 to 50 times. On neutralizing the alkali, as takes place in bating, the plumping diminishes to the same stage as in pure water; further addition of acid renews the plumping. The fallen hide differs from hide which has not been plumped. The fibres have been separated and are ready to receive tanning substances. In addition to the above, the bran bate disengages gas by fermentation, which distends the hide-substance. When following the dung bate, the bran bate also arrests the fermentation which has begun in the alkaline medium. The dung bates have the power of dissolving the interstitial material making the hide porous; this facilitates the removal of the short, deep hairs, lime soap, etc. Pigeon dung leaves the most elastic leather, the action being milder and more uniform for thick hides for which dog dung is not suited, the surface being attacked too rapidly.

Role of Microbes in Bating.—Most of our knowledge of the bacteriology of bates is due to Wood. From bran bate he isolated a microbe which he called *Bacterium furfuris.* This attacks the glucose produced from the starch by a diastase normally present in bran; the cellulose does not ferment. The products of fermentation are carbonic acid, hydrogen and nitrogen gas, lactic, acetic, formic and butyric acids; the total acid is 3 to 4 gms. per litre. Wood supposes that this bacterium is introduced with the hide from the dung bate and finds the bran infusion a favorable medium, contrary to most microbes which cannot resist acids. The question may be raised if the same microbe is present when the dung bate has not been used. The author has isolated a microbe under these conditions, which resembles that described by Wood, but such identifications are difficult. It is probable that the ferments of bran bate vary according to circumstances. Palmer, for instance, in a tannery at Wrexham, found only acids of the acetic series and never lactic acid. In general acids are produced from alcohol, the first fermentation being alcoholic, requiring yeast, and the second requiring the acetic ferment.

Manufacture of Solid Quebracho Extract in Paraguay. *La Halle aux Cuirs*, 1909, No. 9, p. 138.—From a South American journal an account is taken of the manufacture at Puerto-Sastre in the Chaco territory. The forest is situated on the Paraguay River and the factory has the largest installation of any existing in this industry. The power is furnished by steam, operating air and water pumps, saws and grinding mills. The wood is converted into sawdust and chips which is elevated to the third story and delivered into 20 diffusers, each having a capacity of 2600 kilos of wood. Here the extraction with water at 85 to 90° lasts about 50 minutes. The liquor is then settled in tanks for 3 to 4 hours, the leached wood being burnt under the boilers. After drawing off, the liquor goes to the double effect apparatus in the second story where it is concentrated to 25 to 28°B. Next it is transferred to the evaporating pans, remaining 10 hours when it is drawn off at 60-65° as a black paste. This is transferred to sacks and when dried covered with more sacking and is ready for market. 3,000 to 4,000 tons of wood are worked monthly, producing 800 to 900 tons of extract.

Horse Leather Manufacture. *Ledertechn. Runsch*, 1909, Nos. 7, 8, 9; pp. 50, 59, 68. *Soaking.*—After cleaning, fresh hides are thrown into pure water of 15°C, which is renewed the next day. The following morning the hides are further cleaned on the beam and again given fresh water. Salted hides are placed in water of 15° which is replaced 3 or 4 times. Dried hides are softened in water containing 1 kg. caustic soda per cu. metre. The alkali hastens the process without injuring the hide and with fatty hides helps soften and saponify the fats. Normal dried hides may be stretched on the second day, old and hard hides on the third or fourth day. This must be done cautiously with a half sharpened, rounded tool. It is important to thoroughly free the inner side from flesh, fat and blood.

Liming.—With fresh and salted hides, white lime is used, in 3 vats. The hides go first into a twice used lime, remaining 6 to 7 days, then into the once used lime, and then in 6 to 7 days into a fresh lime prepared with 40 to 50 kgs. quicklime to 1 cu. m. water. After 6 to 7 days the hides are ready for dehairing. During liming they are turned every other day; if the room is not protected from light and draft, they should be covered with damp cloths meanwhile. Dried hides are best limed with addition of sodium sulphide 3½ to 5 kg. to 1 cu. m., equivalent to 1 kg. sulphide to 20 kg. lime. Red arsenic (orpiment) is also used, 5 to 6 kg. per cu. m. of liquor. The hides are turned the first day at least 3 times and are ready for dehairing in 4 to 6 days.

Instead of placing the hides after softening in lime vats, they may be piled and treated with a liquor made by dissolving 5 kg. sod. sulphide in 15 litres boiling water and adding 30 litres slaked lime or 60 kg. lime are slaked and 6 to 8 kg. orpiment added. The solutions are diluted with water, but should hang to the hide and not run off the hair. The dehairing can be done on the second day.

Dehairing.—White limed hides are taken from the limes the night before and brought into water of 38° when they fall down. The hair can then be thoroughly removed without strain. Hides from sharpened limes are drummed in running water of 38° for ½ hour to spare the laborers' hands; the dehairing is finished on the beam with a well-rounded tool.

Fleshing and Cleaning.—When shoe-leather is to be made, the hides are separated into shell and forepieces, the first going back 8 days into the white lime. The forepieces are reeled through flowing water for 15 minutes, then piled for 2 days, then split or shaved evenly and finally smoothed with a well rounded tool. The shell pieces after liming are watered ¼ hour at 30 to 35°, stroked on the beam, laid in fresh water of 20° and shorn the next day.

Bating.—The forepieces are watered for 3 days, then rinsed, drained, milled with water of 40° ½ hour and then put in dung bate. Acid is not recommended nor should the bating be prolonged. The shorn shell pieces are watered in the drum and delimed in a weak solution of HCl.

Tanning.—The forepieces are brought rapidly into vats of weak liquor

containing little acid, best provided with reels; the hides are moved continuously at first, then every 10 to 15 minutes. The vats are strengthened the 2d, 7th and 13th days, the foretannage being complete the 18th day. Tanning is completed in the drum in 2 to 4 days, beginning with a liquor of 2°B., increasing to 8°; mixed quebracho and pine extracts are used. The drum should contain as much liquor as possible to prevent lumping and rubbing of the hides. When the leather is tanned through, it goes into a pure concentrated liquor of 5½ to 7°B, remaining 8 days with occasional turning. The shell pieces are tanned with quebracho only, the vat liquors being stronger; in 8 days the hides may be split and next go back to the vats 2 to 3 days, and are finished in the drums with 8° liquor.

The remainder of the paper describes the currying, finishing, etc., in minute detail.

Manufacture of Vache Leather. *Ledertechn. Rundsch.*, 1909, No. 10, p. 73.—Writer softens the hides (salted) 24 hours always in the same water from which the preceding lot has gone to the limes. After cleaning, they are transferred to fresh water which is again changed in 12 hours. After soaking another half day, they are taken out, piled flat, let lie over night and then brought into the limes. The first 2 days, white lime is used, then 2 days a lime with some addition of sulphide, and finally 2 days a lime with addition of ⅓ sulphide. The hides then go into luke-warm water, are then dehaired, washed and shorn. Lactic acid can be used for de-liming. For the first tannage, a series of 10 vats are used, with fresh bark liquors, ½ oak, ¼ pine, ¼ mimosa; beginning with 0.6° B., finishing with 3.5°B; the hides advance one vat daily. A second vat series is then used of 5 liquors, from 4 to 6° B, changing daily. These are prepared from surplus drum liquors, etc. The drum tannage begins with 10°B, moderately warm, for 12 hours, when the liquor is again strengthened to 10°. The strengthening mixture contains 2 parts quebracho, 1 part chestnut, 1 part oak. After 12 hours more drumming, the leather is taken out, and the liquor again strengthened; 24 hours more finishes the process. The hides are taken out, split or cropped and then put into a pit containing a liquor of 12°B at 40°C; they stay here 8 to 10 days with occasional turning. This is for saturation and high yield. The hides are let lie 24 hours after taking out, then put into a liquor of 4° for 1 day, then another day in 2° liquor, and finally several hours in clear water, the object being to remove surplus tans and improve the grain in appearance. The leather is next oiled with kid finish oil, dried and struck out. If bleaching is desired, it can be done as follows: two wooden vessels placed close together are charged, one with a 40°B. solution of ammonia soda, the other with 5°B. oxalic acid, both at 40°C. The hides are drawn through the first solution about 8 seconds, then about 10 seconds through the second and immediately into cold, fresh water. The bleaching is rapid, but requires skillful work. The yield is a leather of 54 to 59%.

Practical Precepts for Drum Tannage of Heavy Leather. *Ledertechn. Rundsch.*, 1909, No. 11, p. 82.—Experience has shown that good leather

cannot be made by the "rapid" process in the drum alone, and that a combination process beginning with a vat tannage is the most efficient. The most important points to observe are:

(1). The vat liquors should not become too acid; a long series is best, beginning with a weak liquor of 1°B. gradually reaching 4°, changing daily or frequently strengthening. Before tanning in the drum, the acids in the hide may be removed by treatment with a weak borax solution, 4 lbs. to a cu. metre, followed by washing in pure water. The hides are then drained on a horse for 12 to 14 hours.

(2). The drum tannage should not begin with too concentrated liquors; it is better to begin with 5°B. and gradually strengthen to 8 or 9°. Mixtures of quebracho extract and oakwood extract are good, also quebracho and pine.

(3). Moderate warming promotes the process, but 36° should not be exceeded.

(4). After leaving the drum, the hides should lie covered for several days; the tans hereby become further fixed and less is lost by washing. 2 to 3 hours watering is sufficient to remove surplus tans and clear the grain.

(5). Oiling the grain with linseed or whale oil is of advantage before drying.

(6). It is better to first work the leather when but half dry.

(7). Bleaching should be applied after drying, the loss being less.

Soda Alum in Tanning. L. MANSTETTEN. *Ledertechn. Rundsch.*, 1909, No. 11, pp. 81-2.—Sodium salts are mostly used in technology in preference to those of potassium, chiefly because of cheapness. This is not however the case with alum, there being no commercial demand for the sodium salt. Recently this has been put on the market in cheap form, and experiments made in the Freiberg Tanning School show that the salt is well suited for tannery use. Its formula corresponds to that of the potassium salt, containing the same amount of water of crystallization, but because of its lower molecular weight, the proportion of alumina is greater, the ratio being 104.3 to 100. This favors its economical use. Its chief advantage is in its much greater solubility. 100 parts water dissolve at

	10°	20°	30°	40°	50°	60°
Soda alum ...	100	125	150	175	200	250
Potash alum..	9.5	15.1	22.0	30.9	44.1	66.6

Below 30° soda alum crystallizes in octahedra, but at higher temperatures becomes an amorphous paste. In making solutions hot water should not be used, but the salt is stirred in water below 30° and gradually warmed with stirring. Experiments were made showing its convenient use for pickling and fore-tanning chrome leather for belting and box-calf. In comparative experiments in tawing saddler's leather whereby the two halves of a hide were rubbed with a mixture of 3 parts alum and 1 part salt, it was found that the leather from the soda alum was heaviest, the

respective rendements being 32.5 and 40%, reckoned on green hide. This is explained by the greater solubility of the sodium salt.

The Use of Talc on Heavy Leather. *Ledertechn. Rundsch.*, 1909, No. 8, p. 62.—This is strewn over the surface of the leather before rolling or beating with a view to lessening the adhesion of the tool and to preserve the smooth surface of the leather. Talc should not be regarded as a dressing to give leather a light color, nor be allowed to collect on the surface. It is best applied with a hand shaker.

PATENTS.

Machine for Mending Imperfections in Patent Leather. U. S. Patent No. 916,124. W. A. DUNBAR, Lynn, Mass.

Pressure Roll for Skiving Machines. U. S. Patent No. 916,037. J. R. SCOTT, Boston, Mass.

Method of Treating Partially Tanned Leather. U. S. Patent No. 916,057. W. H. TEAS, Ridgway, Pa.—Covers the use of extracts, derived in part or entirely from waste sulphite liquors, for stuffing leather previously struck through by an active tanning agent.

Evaporator. U. S. Patent No. 916,054. T. SUZUKI, Sunamura, Japan.

Leather Working Machine. French Patent No. 390,709. AULSON.

Attachment to Leather Working Machine. French Patent No. 390,725. HILL.

Process for Making a Leather Substitute. French Patent No. 390,922. *Schuhfabrik Bonndorf.*—A tissue is covered with several layers of celluloid and subjected to pressure between rollers while still soft.

Process for Transforming Leather into a Whalebone Substitute. French Patent No. 391,002. *Vantajoul.*—The leather is cut to desired shape and plunged successively into baths of water maintained at suitable temperatures, and then dried and pressed.

Leather Working Machine. French Patent No. 393,019. PERKINS AND SMITH.

Method for Decolorizing Tanning Extracts. German Patent No. 206,166. *Badische Anilin und Soda-Fabrik.*—By the use of formaldehyde sulphoxylates alone or in combination with formaldehyde bisulphite. Better results are obtained than with hydrosulphites as described in U. S. Patent No. 376,345.

Method for Purification of Sulphite Cellulose Lye for Tanning Use. German Patent No. 207,776. ALEX KUMPFMILLER.—The free and combined sulphurous acid are converted by ozone into sulphuric acid. The bulk of the calcium sulphate crystallizes out, and the remainder with free acid is removed by barium carbonate. The product besides being a tanning agent, is an excellent material for filling leather.

Tanning Machine. U. S. Patent No. 916,820. F. H. YOCUM, London, Ontario, Canada.

Leather Edging Apparatus. **U. S. Patent No. 917,366.** R. H. SCHWARTZ, Chicago, Ill.

Apparatus for Tanning Hides. **U. S. Patent No. 917,370.** E. F. SMITH, Corry, Pa.

Machine for Applying Liquid to Skins. **U. S. Patent No. 917,683.** W. B. TURNER, Melrose, Mass.

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NOTE ON THE GELATINE-HEMATIN METHOD OF ACID DETERMINATION.

By W. K. Alsop.

The following results may be of interest, especially as the Association is having tested the Gelatine-Hematin method for determining the acidity of tannery liquors.

This table shows determinations made on liquors by this

method, from twenty-three tanneries which are fairly representative as to tanning materials generally used in the sole leather tanneries of this country. In making these tests, a 1 per cent. water solution of gelatine was used for precipitating tannin.

The titrations were made with tenth normal sodium hydroxide, an alcoholic solution of Hematin being used as an indicator.

The results shown in columns 1 to 4 were from samples made by mixing equal volumes of five or six samples of liquor from each tannery. The method followed was as follows:—

To 50 cc. of liquor was added 50 cc. of gelatine solution, the volume made to 250 cc. and kaolin added. After filtering, 30 cc. of the solution was titrated (column 1). The volatile acid was determined by distilling 150 cc. of this solution to 15 cc. and the distillate titrated. This distillation was twice re-

	1 Total acidity as acetic (by gelatine method)	2 Volatile acids				3 Per cent. non-volatile acid. Determined in liquor after distilling as acetic	4 Volatile and non-volatile acids. No. 2 plus No. 3	5 Average acidity routine analyses	
		1st distillate	2nd distillate	3rd distillate	Total				
1	.44	.142	.052	.026	.220	.23	.450	.42	1
2	.41	.130	.056	.022	.208	.22	.428	.41	2
3	.43	.166	.042	.020	.228	.19	.418	.42	3
4	.39	.144	.058	.026	.228	.17	.398	.39	4
5	.40	.162	.060	.026	.248	.18	.428	.42	5
6	.56	.168	.060	.032	.260	.31	.570	.55	6
7	.77	.256	.088	.040	.384	.40	.784	.79	7
8	.54	.236	.080	.034	.350	.23	.580	.54	8
9	.47	.062	.024	.010	.096	.37	.466	.45	9
10	.44	.100	.036	.020	.156	.27	.426	.43	10
11	.26	.064	.026	.012	.102	.17	.272	.25	11
12	.32	.074	.036	.012	.122	.20	.322	.32	12
13	.50	.174	.064	.034	.272	.25	.522	.51	13
14	.24	.026	.014	.002	.042	.18	.222	.23	14
15	.94	.322	.124	.058	.504	.40	.904	.91	15
16	.52	.080	.038	.018	.136	.34	.476	.52	16
17	.76	.130	.068	.032	.230	.47	.700	.75	17
18	.86	.236	.118	.050	.404	.42	.824	.83	18
19	.92	.266	.144	.056	.466	.42	.886	.90	19
20	.95	.190	.078	.048	.316	.63	.946	.97	20
21	.88	.202	.100	.060	.362	.51	.872	.90	21
22	.37	.128	.058	.022	.208	.12	.328	.34	22
23	.37	.096	.054	.024	.174	.20	.374	.36	23

peated after adding 100 cc. of water, each time, to the liquor remaining in the distilling flask.

The non-volatile acid was found after distilling by diluting the liquor in the flask to 150 cc. and titrating 30 cc. The results in column 5 were obtained in the course of routine work and represent the amount of acid shown by averaging that found in the individual samples that were mixed in order to obtain the composite samples used for these experiments.

These routine determinations were made with 25 cc. of liquor and 50 cc. of gelatine solution, diluted to 250 cc. and 30 cc. titrated; or one-half the amount of liquor and the same amount of gelatine that was used for the composite samples. The determinations found in columns 1, 2 and 3 were made by one person, and those in column 5 by another.

Theoretically, the percentage of acidity found should be the same in columns 1, 4 and 5 for each sample, and attention is called to the close agreement shown.

THE ACCURACY OF THE METHOD OF DETANNIZATION OF THE INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMISTS.[1]

By Henry R. Procter.

Considerable doubts have been thrown on the accuracy of the present official method of the I. A. L. T. C. by some German chemists, and especially by the Association of German Extract Manufacturers, who have consistently opposed its adoption, and by implication have thrown doubts on the *bona fides* of the American and English chemists who claimed to obtain exact results. Such complaints were perhaps natural with an unaccustomed process, and especially with an empirical one where absolute adherence to the prescription is essential; and I have hoped that, with experience, the difficulties, and with these the objections of German chemists would disappear. This hope has been largely justified with the individuals, but as the German Extract Manufacturers maintain their attitude of opposition, I feel that it is now time, not only to prove the extreme accuracy of the

[1] From the *J. S. C. I.*

method in capable hands, but to give the fullest possible details of the means by which this can be obtained.

In the first place I will deal with the chroming and washing of the powder, and the obtaining of blank results in which the dry residue of 100 cc. of water shaken with the powder should be under 5 mgr., as prescribed by the regulations, a figure which several chemists have asserted it was impossible to attain. The following is a full description in detail of the method adopted in my own laboratory for the determination by blank tests of the solubles in chromed and washed hide-powder.

The hide powder is weighed, its acidity adjusted, and chromed for one hour according to the I. A. L. T. C. regulations.

The chromed hide-powder is then thrown upon a clean piece of linen in the perforated vessel of a screw-press,[1] or in a funnel, the portions remaining on the sides of the bottle being washed on to the linen with distilled water. The liquid is allowed to drain away, and the powder and linen removed from the press, squeezed by hand, returned to the press, and pressure applied. The more liquid removed at this stage the quicker the powder is freed from chlorides, but care must be taken that pressure is not applied too suddenly, or the linen will burst. The linen with the powder is then removed, and the latter, remaining in the linen all the time, is well broken up by rubbing the cloth between the hands and returned to the press, which is filled up with distilled water. The powder is thoroughly stirred with a glass rod until all the water has run out, and is squeezed again. It is very essential to keep the powder well stirred, otherwise channels will be formed, through which the water will run with very little washing effect. This process is repeated about five times, 50 cc. of the last portion of wash-water which can be removed from the powder by pressing being tested for chlorides. It is advisable after having tested the washings, and found them to comply with the I. A. L. T. C. regulations, to give one more washing, before the final squeezing to reduce the water to the necessary quantity ready for weighing. The washing process should be continuous, and on no account should the powder be left to stand.

[1] The ordinary German fruit-press costing 15s., and holding about one liter, is found to be very satisfactory. It is convenient to have one or two of the inner vessels varying in size for different quantities of powder.

A quantity sufficient for four analyses in duplicate (about 60 grms. air-dried powder) can be washed free from chloride in about 30 minutes, provided the process is continuous. The powder is now ready for weighing, and is transferred from the linen with a spatula to a basin or other convenient vessel for weighing. The last traces of powder may be removed by holding the four corners of the linen together and beating it upon the bench, when the powder will collect in the centre of the cloth. The remaining manipulations are precisely as for tanning analysis, but using 100 cc. of distilled water instead of tanning liquor.

The following causes tend to too high residues when carrying out blanks:—

1. *Impurities in the distilled water used.*—The distilled water should leave no weighable residue on evaporation of 100 cc. to dryness.

2. *Soluble matter from the hands* when squeezing the liquid away from the powder after detannization. The powder in the linen might be pressed against the side of the funnel with a spatula to expel the last of the liquid.

3. *Soluble matter from linen* used after final churning. The cloths should be washed with water alone, nothing in the nature of soap being used, and finally in distilled water before drying.

4. *Imperfect insolubility of the kaolin* used. This has caused serious errors, and the kaolin should be tested before use.

5. *Presence of dust* with the residue in the basin.—The evaporation should be carried out with as little access to dust as possible, and the basin should be tranferred to the drying oven as soon as possible after evaporation is complete.

The following table gives the results of such blank experiments with different powders. The determinations in columns I. and II. were executed by various assistants, and those in column III. by students doing tannin analysis for the first time. The results are not selected for accuracy, but contain the whole of the determinations executed at that time under the respective heads. It was subsequently found that the distilled water was not qute satisfactory, but left a residue of 0.0004 grm. which should be deducted from each determination. Similar experiments were made with a sample of Freiberg powder with less

satisfactory results, which are not quoted, as no doubt the quality of the powder has since been improved.

RESIDUE FROM 100 CC. OF BLANK EXPERIMENTS.

American powder. I. Grm.	Vienna powder. II. Grm.	Vienna powder. III. Grm.
0.0023	0.0003	0.0042
0.0026	0.0000	0.0042
0.0013	0.0020	0.0036
0.0006	0.0036	0.0040
....	0.0030	0.0048
....	0.0020	0.0040
....	0.0023	0.0046
....	0.0036	....
....	0.0026	....
0.0017	0.0022	0.0042 average

The importance of giving at least one additional washing and squeezing after the powder is freed from chlorides sufficiently to answer the prescribed chromate test is shown by the following results. Probably if the amount of N/10 silver nitrate allowed were reduced from 4 to 2 drops per 50 cc. sufficient washing would always be attained.[1]

	After chlorine test. Grm.	One additional washings. Grm.	Two additional washings. Grm.
Residue from.....	0.0060	0.0033	0.0030
100 cc. of distilled.....	0.0063	0.0023	0.0016
Water shaken with powder	0.0040	0.0010	0.0013
	0.0054	0.0022	0.0020

As regards concordance of analyses, the following figures may be given with regard to 31 analyses carried out in the University Laboratory by various analysts to test whether any difference in results existed between American and Vienna powders. These analyses were done in the course of ordinary commercial work with no greater attempt at accuracy than is made with every analysis which is executed, and each figure represents a complete pair of duplicate analyses, such as are always done for commercial purposes; and they include the whole of the analyses

[1] The test of four drops of $AgNO_3$ amounts to about 2.3 mgr. NaCl on 50 cc. of the wash-water. No doubt on making a blank test by shaking with only 100 cc. of water, a larger proportion would be obtained. In case of doubt it is therefore wise to make such a blank test on the actual powder which is afterwards used for analysis.

done to compare the powders without selection or rejection, and embrace sumac, lentiscus, mimosa and mangrove barks, chestnut, and oakwood extracts.

They are therefore in no sense "parade analyses."

RESULTS WITH AMERICAN AND VIENNA POWDER.

Non-tannin Residue from 60 cc.

Material.	Grms. per liter.	American powder.	Vienna powder.	Differences to Vienna. +	American powder. −
Sumac	15	0.1210	0.1210	—	—
"	15	0.1192	0.1198	—	0.0006
"	15	0.1246	0.1230	0.0016	—
"	15	0.1224	0.1220	0.0004	—
"	15	0.1246	0.1232	0.0014	—
"	15	0.1194	0.1194	—	—
"	15	0.1242	0.1236	0.0006	—
"	15	0.1268	0.1270	—	0.0002
"	15	0.1166	0.1188	—	0.0022
"	15	0.1170	0.1192	—	0.0022
"	15	0.1190	0.1204	—	0.0014
"	15	0.1196	0.1190	0.0006	—
"	15	0.1194	0.1190	0.0004	—
"	15	0.1210	0.1212	—	0.0002
"	15	0.1220	0.1230	—	0.0010
Lentiscus	24	0.2296	0.2310	—	0.0014
"	25	0.2410	0.2418	—	0.0008
Mimosa	11	0.0534	0.0548	—	0.0014
Natal Mimosa	10	0.0758	0.0746	0.0012	—
" "	8	0.0760	0.0730	0.0030	—
" "	9	0.0772	0.0774	—	0.0002
" "	8	0.0728	0.0756	—	0.0026
Mangrove bark extract	6	0.0788	0.0794	—	0.0008
Oakwood extract	16	0.1438	0.1418	0.0020	—
" "	16	0.1362	0.1366	—	0.0004
" "	14	0.0468	0.0464	0.0004	—
" "	15	0.1214	0.1212	0.0002	—
" "	15	0.1128	0.1128	—	—
" "	15	0.0928	0.0910	0.0018	—
" "	15	0.0876	0.0872	0.0004	—
Chestnut extract	13	0.0504	0.0500	0.0004	—
Total No. 31 analysis	—	3.5132	3.5142	0.0144	0.0154

Sum	0.0298
Difference	0.0010
Mean	0.00096

To sum up results, it may be observed that the greatest diver-

gence in any pair is 3 milligrams, which in an oak-wood extract corresponds to about 0.13 per cent.; the mean difference is under 1 milligram, including errors both ways; and the total sum of the differences, subtracting those on one side from those on the other, is under 1 milligram. This proves that detannization by shaking with hide-powder according to the I. A. L. T. C. prescription is a method of great accuracy, and quite as exact as any ordinary chemical determination such as that of moisture by drying, and that two different hide-powders of good quality separately chromed and washed and brought to the same standard of acidity will give absolutely identical results. Now this detannization is the only point in which the present official method differs from the old one, and so far as my experience goes, it is impossible to produce a series of the same concordance by the filter method with any powder, however carefully prepared.

It may be urged that all this does not prove that different analysts with different samples will get results of corresponding accuracy; and I agree that it does not. No imaginable method will avoid the frequent errors which arise from inexact sampling by clients, and no method will prevent the carelessness and incompetence of unconscientious chemists, but the results quoted show that such differences are avoidable by skill and careful work, and do not depend on differences of hide-powder, or any cause beyond the control of the chemist.

It has been suggested, that while analyses done by a chemist as duplicates show a satisfactory concordance, it is difficult for him to repeat the result at some future time; and it is is impossible to prove that this is not the case, especially if a new sample must be drawn, since few extracts remain constant in strength, but differ in solubles and tannin by fermentation and by settling of the difficultly soluble constituents, so that no two samples taken at different times can be guaranteed to be absolutely alike. Solid extracts also vary in moisture and possibly in solubility, and fair sampling even with the greatest care is by no means easy.

The following non-tannin determinations, however, in which analysis of the same solution was conducted by different assist-

ants, each chroming their own hide-powder and in ignorance of each other's results, prove that the determination of non-tannins at least will agree if performed on identical materials. Here again all results good and bad of a series are quoted.

RESULTS OF REPEAT ANALYSES CARRIED OUT BY INDEPENDENT OPERATORS.

Material.	Grs. per Litre.	Per Cent.	Per Cent.	Operator.
Sumac "40"	15	0.1216 = 16.21	0.1212 = 16.16	H. Br.
		0.1214 = 16.18	0.1210 = 16.13	W. J.
Extract "54" contains	14	0.0636 = 9.08	0.0632 = 9.02	S. H.
Fichtenholz extract...		0.0624 = 8.91	0.0616 = 8.80	H. Br.
Extract "333"	14	0.0666 = 9.51	0.0658 = 9.40	S. H.
		0.0660 = 9.42	0.0662 = 9.45	W. J.
Quebracho extract	6	0.0318 = 10.60	0.0308 = 10.26	S. H.
(solid) "2628"		0.0330 = 11.00	0.0332 = 11.06	W. J.
Quebracho extract	6	0.0312 = 10.40	0.0318 = 10.60	S. H.
(solid) "2563"		0.0322 = 10.73	0.0306 = 10.20	W. J.
Swedish Fir Bark ex-	22	0.2336 = 21.23	0.2334 = 21.12	W. J.
tract		0.2336 = 21.23	—	W. J.

As a further test of the comparative accuracy of the official determination of non-tans, I applied to a number of English extract manufacturers and large dealers whom I knew to have been making extensive tests of the concordance of the results of different chemists under the new method, for information as to the results obtained; and received in all, details of the analysis of 20 different extracts each determined by two or three different chemists, of whom in many cases I do not even know the names. In order to determine the degree of concordance attained the average result on each material was determined, and the sum of the differences from these averages was taken without regard to whether + or — . One set of three analyses was rejected on account of an obvious clerical error in one analysis which added to 102.3. Of the remaining 51 analyses the average difference from the mean was 0.39 per cent. In order to compare to some extent the accuracy of the work and sampling, the water determinations of the same extracts were similarly compared, and showed an average error of 0.31 per cent. As a further check, the non-tannin results of the 66 analyses by the filter method with Prof. Paessler's "lightly chromed powder" carried out by Messrs. Arnoldi, Bosch, Moll, Phillip, Sichling, Seidel, and Veit for the

German Analysen-commission, and published in the report by Prof. Paessler (*Collegium,* 218, et, seq., 1908), were similarly treated; and showed an average error of 0.42 per cent. As in this case the samples were sent out as identical by Prof. Paessler himself, together with an identical hide-powder, and the names given preclude the supposition of careless or incompetent work, while those by the shake method were by ordinary commercial chemists, with commercially drawn samples, and any hide-powder, the comparison of the results is interesting.

Most of the extract manufacturers now admit that present results by the shake method show better concordance than the former with the filter, and several of the more important are warm supporters of the change; and complaints now centre rather on the defects of colour-testing than on the actual tannin determination.

In conclusion I may say that the evidence I have brought seems to me absolutely to establish the superior accuracy (or at least concordance) of results of the shake method as compared either with the old filter method, or with Dr. Paessler's with lightly chromed powder, and though, as Chairman of the Commission, I shall be glad to discuss any improvements which may be suggested either in accuracy or rapidity of execution, I consider that the controversy as regards the superior accuracy of the old filter method is now closed so far as I am concerned.

SPEW ON LEATHER.[1]

By Rowland A. Earp, B.Sc.

Most men familiar with the handling of leather must occasionally have come across samples showing a whitish scum, or spew, upon the surface. Tanners frequently experience it in some form or other in the drying shed, and especially in the warehouse; whilst I have known a parcel of leather to generate a spew at every halt in its course through the hands of brokers, factors, manufacturers, and retailers. It is with reference to this phenomenon that I wish to devote this article.

Spew (from an old Anglo-Saxon word, meaning to vomit)

[1] From the *Leather Trades Review.*

is an occurrence almost confined to leather. It is, indeed, to the leather trade that we owe the preservation of this word, for its other uses in English language have almost dropped out. Literally, the word signifies something that is expressed or has exuded from the interior of the leather substance, and many spews are of this nature; but frequently we come across spews which are more in the nature of surface growths, and are no more a rejected portion of the leather than we can say a moss is a rejected portion of the stone upon which it grows.

THREE MAIN CAUSES OF SPEW.

There are three main causes of the occurrence. which give rise respectively to the three typical classes of spews. Perhaps the most frequent kind is a species of a low type of organic growth. This makes its appearance on the leather whenever the conditions are favorable for a fungoid growth, such as moistures and septic. The spew takes varying forms, for the number and variation of these low fungi are very great. It may appear as a whitish scum, of a nature similar to the bloom on fresh fruit, or it may assume a more developed organic structure similar to that of blue mould.

The second kind of a spew is of the nature of an efflorescence, and occurs in leathers which contain a large amount of a crystallizable salt. It makes itself visible by means of the alternations in degree of humidity of the atmosphere, a damp atmosphere bringing the salt to the surface and a dry atmosphere causing it to effloresce there.

The third kind of spew is the result of a partial decomposition of the substance to the leather, and this kind varies very much in appearance. The effect of the decomposition may result in one of the products being thrust out on to the surface, or some other constituents may be thrust out. Again, the decomposition, though not resulting in anything being actually thrust out on to the surface, may yet cause the surface to become discolored or otherwise changed in appearance.

FUNGOID SPEWS.

These spews occur on all leathers, both genuine and adulterated.

Genuine leathers do not readily give off this spew; but on long storage, especially in a damp room, the best leather will become coated with the spew. On some classes of adulterated leather this spew is specially insistent, and for this reason an insistent spew is generally regarded as an indication of adulteration. Quite correctly so; but it does not follow that because a leather does not spew that it is not adulterated. It is comparatively a simple matter to adulterate leather to a great pitch, and yet to make it as little liable to spew as the best leather. The main condition necessary for its formation is dampness. It is also induced by the presence of certain matters within the leather which are nutritive to its growth. The fact that some adulterants are hygroscopic, and therefore cause the leather to become damp, and also that some are nutritive, very often cause adulterated leather to be especially liable to this form of spew. The obvious remedy, and one that the intelligent sophisticator follows, is the application of an antiseptic sufficiently strong to prevent any organic growth.

It is not often that real harm to the leather is caused by this form of spew, though, if neglected for too long. considerable harm may be done. The presence of the spew is an indication of dampness of the leather, and damp leather in pile is apt to become heated. The growth itself is always associated with certain ferments tending to liquefaction of the constitutents of the leather, and it should be kept back by regularly wiping it off.

EFFLORESCENT SPEWS.

This spew is the *bête noir* of tanners who adulterate with inorganic salts, for it can only appear on leathers which contain them. Notwithstanding how carefully the grain of the leather may have been cleared from the adulterating material, it slowly diffuses out from the interior, especially during damp weather, and it is then liable to become visible through the phenomenon of efflorescence. The efflorescence is a result of the leather becoming so dry that the enclosed adulterating salt can no longer be held in association with the leather. The phenomenon of efflorescence may be seen on leaving a crystal of common washing soda exposed to the atmosphere for some days. It becomes

covered with a flowery "spew." Although damp weather is favorable to the transference of the salt to the surface, dry weather is required to make the salt effloresce; and alternations of dry and humid atmospheres especially favor its formation.

There are two ways of preventing this spew. One is to convert the salt into an insoluble form within the leather, and thus make it independent of any external atmospheric variation. The other means is more practical, and consists in associating with the mineral salt some substance which acts as a carrier of moisture, and thus behaves as a cushion in preventing the extremes of the variation of the atmospheric humidity from affecting the disposition of the salt.

SPEWS RESULTING FROM DECOMPOSITION OF SUBSTANCES WITHIN THE FIBRE.—ERUPTIVE SPEWS.

These spews are very varied. They are related to the first class mentioned, in that the change in the interior of the leather is generally a fermentative, or organic one. Similarly, also, with the first class, it is found that moisture and a mild temperature favors the formation of the spew, for no decomposition can arise unless the leather is in a damp condition. The constituents of the leather which give rise to the spew are always of an organic nature, and are, as a rule, only loosely held by the leather fibre. It is not often that lightly-tanned leather spews, but heavily-tanned leather, or leather containing an excess of readily fermentable tans, or leather loaded with organic filling materials (generally highly fermentable), are subject to this spew. In fact the spew is strikingly suggestive of the result of overloading one's stomach with rich and indigestible food.

Under this class may be included all the fatty spews which occur on the surface of curried leather. Mr. F. Jean (*Collegium*, 1907, pp. 363-366) gives an instance of the spew occurring on curried leather in the form of "little yellow, transparent, resinous drops" upon the surface, and attributes it to the action of moisture, heat, and ferments.

Another example of an eruptive nature is the following. It has especially come under the writer's notice and is a very annoying occurrence met with in currying. It consists in the layer of grease applied to the surface of the leather refusing to

stay on and dropping off on to the floor. It is due to a spew of carbonic acid gas, which is generated through fermentative change in the interior of the leather, and which in its escape blows off the layer of fat. The spew is easily prevented by the use of a suitable antiseptic.

There are a great number of cases where the surface of the leather, upon lying in store, becomes irregularly discolored. These discolorations, although not spews strictly speaking, are of a similar nature to the occurrences now under discussion, the difference being that instead of the products of decomposition being thrust on to the surface, they remain *in situ*, or, at any rate, do not get further than the interior surface.

PREVENTION OF ERUPTIVE SPEWS.

In order to prevent these spews the leather must be kept in an aseptic condition. Dryness alone is a sufficient preventive against internal decomposition, and finished leather, if kept quite dry, will not spew; but spews occurring during the drying of the leather are only to be dealt with by antiseptics. Indeed, there is little doubt but that if the whole process of tanning and finishing were carried out on aseptic principles, other unpleasant occurrences, besides spews, would be largely prevented.

The tendency to become damp, or hygroscopicity of leather, considered with relation to spew formation, together with some general remarks upon this important property will be dealt with in a separate article.

ABSTRACTS.

The Composition of a Series of Vat Liquors. F. MERKEL. *Ledertechn. Rundschau*, 1909, No. 12, pp. 89-90.—The practice in the Freiberg Tanning School is to make analyses of the liquors at regular intervals for the purpose of control. The writer gives tabular results of such analyses for a practice of three years. The tanning system consists of a series of 10 vats of 5 cu. m. capacity, provided with press-logs, the liquors circulating on the pressure principle, being finally discharged from the weakest vat; 12 to 15 hides are entered at one time. For liquors, pine bark, mimosa, maletto and some myrabolams were principally used as well as the draw-off liquors from the finished tannage, being mainly oak, mimosa, valonea, together with quebracho extract. Acid determinations were made

monthly and complete analyses twice a year. We reprint one each of the two sets of tables.

TABLE III.—SCHOOL YEAR 1908-9. AVERAGE ACID CONTENTS AS ACETIC ACID.

	Vat number									
	1	2	3	4	5	6	7	8	9	10
Apr.	0.22	0.34	0.35	0.36	0.37	0.38	0.39	0.39	0.39	0.39
May	0.23	0.33	0.35	0.35	0.35	0.36	0.37	0.38	0.38	0.37
June	0.25	0.36	0.39	0.39	0.39	0.39	0.40	0.41	0.42	0.41
July	0.33	0.40	0.43	0.43	0.44	0.44	0.46	0.46	0.47	0.46
Aug.	0.27	0.43	0.47	0.51	0.55	0.54	0.58	0.57	0.59	0.60
Sept.	0.24	0.45	0.51	0.54	0.55	0.58	0.59	0.59	0.59	0.58
Oct.	0.31	0.46	0.53	0.55	0.57	0.56	0.56	0.55	0.52	0.50
Nov.	0.25	0.42	0.49	0.50	0.51	0.51	0.52	0.52	0.52	0.52
Dec.	0.28	0.40	0.45	0.47	0.47	0.47	0.47	0.47	0.47	0.47
Jan.	0.17	0.33	0.38	0.42	0.44	0.45	0.44	0.44	0.44	0.43
Feb.	0.15	0.28	0.33	0.39	0.39	0.40	0.41	0.42	0.43	0.43
Mar.	0.19	0.25	0.32	0.38	0.39	0.41	0.41	0.42	0.42	0.42

TABLE V.—ANALYSES OF SEPT. 2, 1907.

No. vat	Specif. grav.	Total acid as acetic	Volatile acid as acetic	Non-volatile acid as lactic	Organic		
					Total extract	Non-tans.	Tans
1	1.0093	0.47	0.27	0.29	2.01	1.42	0.59
2	1.0100	0.57	0.29	0.41	2.18	1.42	0.76
3	1.0105	0.62	0.32	0.45	2.39	1.43	0.96
4	1.0110	0.63	0.31	0.45	2.53	1.46	1.07
5	1.0116	0.62	0.30	0.47	2.74	1.41	1.33
6	1.0132	0.64	0.26	0.54	3.17	1.41	1.76
7	1.0145	0.67	0.29	0.57	3.43	1.62	1.81
8	1.0155	0.68	0.29	0.57	3.74	1.55	2.19
9	1.0160	0.69	0.28	0.60	3.90	1.50	2.40
10	1.0160	0.68	0.25	0.65	3.91	1.40	2.49

Vat No. 1 was the weakest and subjected to more irregularity, the hides entering here. In the first series, it is seen that the acid content varies with the season, increasing with the temperature. The strength of the tanning liquors shows a regular gradation in the second series of tables. The record is given as a demonstration that it is desirable and possible to maintain a certain regularity in manufacture even in such a small plant as that of the Tanning School operating with miscellaneous materials and extracts.

Cutch and Gambier. W. EITNER. *Der Gerber*, 1909 [35], Nos. 830, 831; pp. 85, 99.—The use of these materials has increased greatly in recent years owing to the demand in combination tanning, and especially in making leather for dyeing. Although obtained from very dissimilar plants, the active tanning substance is the same in each, namely catechu-tannic acid. This dissolves readily in water of 25° and tans the hide through rapidly. Another ingredient is catechin which does not tan and is insoluble in cold

water. As obtained from gambier, it is more crystalline than the form obtained from cutch (japonica). Both materials are obtained from India, Ceylon and Malaysia. Cutch is leached from the wood of an acacia and the extract concentrated to a thick syrup, poured out into forms and let harden and further dry in the sun. Gambier is similarly obtained from the leaves and twigs of a climber of the *Rubiaceae* family. The dried extract comes in the form of blocks and in smaller dimensions as cubes, these last containing less water. Gambier extract is now made according to modern processes, appearing in the market as Indragiri gambier (This JOURNAL, 1909 [4] No. 1, p. 25). This dissolves completely in boiling water but gives a considerable sediment on cooling and standing consisting principally of catechin.

ANALYSES.

	Indragiri gambier	Cube gambier	Block gambier			Japonica cutch	
Tans	39.70	50.34	36.80	37.66	39.56	50.65	52.68
Non-tans	22.62	29.56	22.44	24.10	26.80	26.28	23.54
Water	35.87	12.36	35.40	27.83	27.08	12.45	11.93
Insoluble	1.81	7.74	5.36	10.41	6.58	10.62	11.85
Ash	3.77	3.42	3.26	4.73	2.20	7.27	
Recomputed for 35.87 Water in Each:							
Tans	39.70	36.84	36.83	33.47	34.79	35.13	38.37
Non-tans	22.62	21.63	22.44	21.41	23.51	20.25	17.14
Insoluble	1.81	5.66	5.36	9.25	5.83	8.75	8.62

Comparisons may best be made from the lower table.

Gambier is preferred to cutch, giving a fuller leather, with a better feel. This is explained as due to the more crystalline character of the catechin deposited in the fibre; this is demonstrated by producing a similar effect with Epsom salt. On account of the high price of these substances, substitutes are used, one of the best being R-catechu, manufactured by Paul Gulden, Leipzig, containing 60% tanning substance.

Remarks on the Tanning of Plumped Hides. L. MANSTETTEN (Freiberg Tanning School), *Ledertechn. Rundschau*, 1909, No. 15, p. 114.—In sole-leather tanning, an undesirable product is frequently obtained, which on cutting, shows light colored within, while the outer layer is dark. This is not due to incomplete tannage, for examination shows the inside to be well tanned. A ready explanation would be that the tanning had been completed with light colored tan-stuffs. The author, however, believes the fault is due to the plumping, for the following reasons: The defect is confined almost wholly to sole-leather, which is plumped the most. Other heavy leathers, although tanned with the same materials, seldom show the uneven color. It is probable in the case of sole-leather, that the swelling is pushed too far in advance of the fore-tannage, and the insufficiently tanned hide is brought into too strong a liquor. Experiment has shown

that when the fore-tannage has been made to proceed more gradually, the fault in question has disappeared. This all goes to show how important it is to conduct a tanning process rationally. The question is often asked how far the handler tanning should proceed before shifting to the lay-aways. There can be no absolute answer to this, since the two stages are mutually dependent and either may be modified to suit the other. In general, those materials weak in tans contain relatively much non-tans and are best suited for leathers which have been but slightly fore-tanned. This is in accord with the ancient tanning process. With modern methods, employing foreign materials rich in tans, but containing little acid-forming non-tans, it is necessary to use ready acids for the plumping to obtain a uniform and gradual fore-tannage.

Temperature in Liming. L. MANSTETTEN, (above).—The practical processes for increasing the depilating action of the limes by adding old, fermented limes or by "sharpening" with sulphide, are much affected by temperature. Writer recommends 16 to 18°C.; 20° should not be exceeded except with caution. Instead of strengthening a lime with more sulphide, the same result may often be obtained by warming judiciously.

The Role of Microbes in the Putrefaction of Hides. M. G. ABT (ante, p. 165), reprint, *LaHaile Aux Cuirs,* 1909 [53], Nos. 15, 16, 17, 18, pp. 237. 255, 271, 289.

Dung Bates.—No special study has been made of fowl dung, so it is included in the same discussion with the bate from dog dung. According to what is published, it is well that the dung be fermented before preparation of the bate. Dog dung should be kept in a rather liquid paste for 15 days to 3 weeks according to Borgmann and for 1 to 3 months according to Wood. The nitrogenous matter decomposes to at least the stage of amino-acids. In the bate, these ammonia compounds from the dung, together with analogous substances formed at the expense of the hide, dissolve and remove the lime. Employed alone, however, they do not act as in the bate. Both Eitner and Wood have shown this with sterilized bates and solutions of aniline salt; the hide is not attacked. Wood isolated the diastases secreted by the microbes from a bate of dog dung and ascertained that they completed the action of the amino-products. We are far from knowing the microbes which produce these diastases. Probably they vary; some 40 to 50 species have been isolated from dung, of which many attack albumen. In bates, however, only 4 or 5 species have been isolated at one time. Popp and Becker have separated a species of *Coli* which they call *Bacillus erodiens;* it produces gas and can ferment sugar; it does not liquefy gelatine but develops a disagreeable odor in peptonized media. It develops moderately at 22° but rapidly at 37° although the culture is stationary after some hours. It appears to be relatively little active for Popp and Becker recommend in using it in Erodine, to give sheep and goat skins an additional day of liming. Wood's best results were obtained by a mixed culture of two microbes isolated from the hair roots in the sweating process. Separately, these had little action on hide, but in mix-

ture gave a very active bate. Here, as in other cases, the most favorable microbes do not liquefy gelatine. It would seem that their action on albumen must be limited. On the whole, researches thus far, do not suffice to explain what goes on in the bate.

Erodine.—This is a substitute for dog-dung bate, furnished commercially. It consists of a pure liquid culture and a solid substance used in preparing the medium. Of this solid, 10 grams are taken to each kilo of white hide, mixed with 50 parts of water at 40°, the culture added and the whole left to ferment 5 days. The method has met with some success with calf and sheep skins, but has not come into general use.

Control of the Bate.—Bran bates may be kept relatively pure, at least when careful oversight is taken. After a bate has been emptied, other microbes than the *Bact. furfuris* may develop on the walls of the vats and are doubtless the cause of most mishaps. The practice of washing and brushing the vats between each operation, is to be commended. The temperature is important and should not exceed 30°. Butyric fermentation of the bran bate is much dreaded. It develops very rapidly during thunder storms, perhaps because of the increase in temperature and may progress to solution of the hides.

It is important that the material for the dung bate be preserved in good condition, particularly dog dung, which easily deteriorates if not perfectly dry. The damaged part is recognizable by its color and is best removed. Herr Borgmann of the Freiberg School, recommends its employment as follows: A paste is prepared in a sterilized cask 2 or 3 weeks before use, the whole being covered and left to ferment. When required, an extract is made with warm water and only the clear liquor is used, after straining. A temperature of 32 to 35° suffices in preparing the bate and may be raised to 37 or 38° before putting in the hides. Eitner recommends for glove leather, according to thickness, 23 to 34°. The bating is shortened by a previous washing of the hides, which is very efficient when sulphide has been used in depilation. Hides which have, however, suffered in the soaks or limes, spoil rapidly in the bate, and it is best then to omit washing. Frequent stirring during bating is necessary.

The Employment of Different Bates.—So long as the effect of bates is uncertain, their use should be avoided unless indispensable, relying upon acids; otherwise resort may be had in order of frequency to bates of bran, fowl dung and dog dung, the last being to avoid the most. The danger of growth of injurious microbes may be lessened by shortening the process, using acids at the same time. In this way, the bran bate is preceded by a washing with formic or lactic acid, which removes most of the lime. With the dung bates, the acid treatment is more reliable after bating. The pickling process with salt and acid, is well suited for chrome tanning and even for vegetable tannage with rather concentrated liquors. Only in the case of goat skins and the small pelts used in glove making, is a bate of dog dung indispensable.

How to Arrest a Bate.—When a butyric fermentation has set in, chalk

may be added, or borax. An addition of 10% salt produces with the acid a pickle and arrests the fermentation. If it is possible to withdraw the hides, this is best, and they may then be placed in a pickling bath. This would also be the logical treatment with a dung bate. An antiseptic treatment has also been proposed, a naphthol solution being used.

School of the Tanner (continued); **Object of Plumping.** A. SCHMIDT, *LeCuir*, 1909 [2], Nos. 6, 8, pp. 119, 171.—The swelling produced by acids is different from that which takes place in the limes. While nothing is known of the actual nature of the phenomena, it is certain that a plumping by alkalies cannot directly precede tannage.

The object of the normal plumping with acids is to put the hide into a condition for absorbing the maximum amount of tannin. The crude hide may be considered as a felted mass of interlaced fibres nearer parallel to the surface as the grain is approached. In dried, thin hides, these fibres are glued together. On swelling, the water fills spaces between the fibres, increasing the thickness of the hide; this permits the penetration of the tannin and its maximum absorption. There is a definite limit, however, to the fixation of the tannin by the hide substance itself, namely equal weights of each. Beyond this is supercharging with unfixed tannin, removable by washing. The plumping also increases the rapidity of the tannin absorption and exposes the maximum surface of hide fibre. To gain these advantages, however, plumping should not be pushed beyond a certain limit. If the fibres are distended beyond their natural elasticity a partial rupture takes place which is permanent and may be detected by the microscope. Such leather has lost in strength and compactness and has a spongy texture.

(To be Continued.)

A New Concentration Apparatus for Extract Manufacture. RICHARD RIEDER (Patent applied for), *Der Gerber*, 1909 [25], No. 830, p. 86. This apparatus, called "The Multiplex," is the design of the inventor of the extractor "Automat." It may be operated by direct or exhaust steam, which is utilized successively in three members, and yields hot water suitable for employment in various operations of the tannery. The concentration terminates in a vacuum at 50° to 85°C.

Carbon Tetrachloride in Varnish Preparations. *La Halle aux Cuirs*, 1909 [53], No. 16, p. 258.—This is an excellent solvent for many gums insoluble in alcohol. A good varnish is made by dissolving dammar at 120°F.; this gives a hard, transparent coat, more durable than when spirits of turpentine are used. Such gums as lac, sandarac, etc., give a clear solution in watered alcohol on addition of 10 to 20% carbon tetrachloride.

PATENTS.

Leather Shrinking Machine. U. S. Patent No. 917,857. A. FAIFER, NEW York.

Gage for Skiving Machines. U. S. Patent No. 920,823. M. CAVANAGH, New York.

Vacuum Pan. U. S. Patent No. 920,997. G. R. RAY, Manistee, Michigan.

Leach Casting Machine. U. S. Patent No. 921,021. J. J. STEHLING, Milwaukee, Wis.

Method of Coating Leather With Fabric. U. S. Patent No. 921,229. F. J. GLEASON, Walpole, Mass. Consists in providing the fabric with a coating of rubber or rubber compound, then subjecting the coating to the action of carbon tetrachlorid, and finally uniting the fabric to the leather.

Leather Finishing Machine. U. S. Patent No. 920,304. A. G. FILMER, Gloversville, N. Y.

Process for Preparing Hides for Tanning. French Patent No. 384,498. HENRI BOULANGER. This consists in direct treatment of the crude hides with weak tanning liquors, permitting in time a removal of the epidermis, hair and other waste without decomposition of the hide itself which is liable in the usual liming process.

Machine for Dyeing Leather. French Patent No. 391,717. SOC. BILLAND, FILLIAS ET CIE. The hide is automatically removed after making the desired number of passages before a brush applying the tint.

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ELECTIONS

Mr. S. Boyd Gunnison, Erie, Pa. (From Associate to Active.)

THE GELATINE-HEMATIN ACID METHOD.

By W. K. Alsop.[1]

In accordance with a request of the Council about 45 members of the Association were asked to collaborate in testing the Gelatine-Hematin method of determining acidity in tanning liquors. To such as expressed a willingness to participate in the experiments, samples of liquor were sent as follows:

No. 1—Acid hemlock	31	degrees	barkometer,	about 3.5%	tannin
No. 2—Acid hemlock	18	"	"	" 1.5%	"
No. 3—Oak	39	"	"	" 4.25%	"
No. 4—Oak	28	"	"	" 2.5%	"
No. 5—Mixed	31	"	"	less than 1.0%	"
No. 6—Mixed	10	"	"	about .5%	"

One cubic centimeter of formaldehyde solution to 1000 cc. of liquor was put in each sample, except No. 5, to which chloroform had been added. The acidity was determined at the time these samples were sent out, March 29th;

No. 1	.81%	as acetic acid
No. 2	.82%	"
No. 3	1.14%	"
No. 4	1.02%	"
No. 5	.62%	"
No. 6	.14%	"

The directions for experiments and part of the letter accompanying them, were as follows;

DIRECTIONS

1. Alcoholic gelatine solution. Neutral to hematin. See under experiment No. 3 for proportion of gelatine, alcohol and water.

2. One per cent. water solution of gelatine neutral to hematin.

3. Hematin solution, .05 per cent. My method of preparing the solution is to digest the hematin in cold 95 per cent. alcohol, in the proportion of .5 gr. to 100 cc. alcohol. This is used without filtering.

4. Acid washed kaolin. Free from soluble matter.

5. Tenth normal sodium hydroxide.

EXPERIMENT NO. 1

To 25 cc. of liquor, in a cylinder that can be stoppered, add 50 cc. of alcoholic-gelatine solution. Dilute with water to 250

[1] Report of 1909 Committee.

cc., add 15 grams of kaolin and shake vigorously. After allowing to stand 15 minutes for precipitate to settle, remove 30 cc. of liquor, whether clear or turbid, dilute to 75 cc. and titrate with normal soda, using hematin for indicator.

EXPERIMENT NO. 2

Proceed as in No. 1 using water solution of gelatine instead of the alcoholic solution.

EXPERIMENT NO. 3

Proceed as outlined by H. C. Reed in JOURNAL A. L. C. A., Vol. 3, No. 3, Pages 85-87.

"Inclosed are directions for three sets of experiments. Numbers 1 and 2 are practically the methods that have been used in this laboratory for nearly a year. Experiment 3 is a request for determinations according to Mr. Reed's original directions; the amount of liquor and gelatine to be used being left somewhat to the judgment of the analyst.

The method of neutralizing alcoholic or water solutions of gelatine used here is as follows:—After the solution is made to the volume required 50 cc. is removed with a pipette, diluted to 250 cc. and titrated with standard alkali or acetic acid, as may be necessary, using hematin as indicator. The amount of acid or alkali required is calculated for the rest of the solution and added.

I agree with Mr. Reed that the use of hematin as an indicator requires a certain amount of practice. The color changes are not always the same, varying from red to blue. This depends largely upon the character of the liquor being tested. I would suggest that anyone not familiar with the method make one or more titrations before making final determinations. The amount of hematin solution used should be about ½ cc., although this may occasionally be varied somewhat to advantage.

I would be pleased to have results of other tests or experiments than those outlined. Kindly report results at your early convenience, not later than May 1st. Aso please give full expression to your views concerning the method."

Following are tabulations of such results as were received prior to June 12th. The acidity is expressed in all cases as the per cent. of acetic acid by volume.

SAMPLE 1.

Analyst	Experiment 1 acidity as acetic acid	Experiment 2 acidity as acetic acid	Experiment 3 acidity as acetic acid	Experiment 3 cc. liquor used	Experiment 3 cc. gelatine used	Experiment 3 cc. dilution	Experiment 3 cc. for titration	Experiment 3 cc. N/10 NaOH
R. H. Wisdom	.84	.76	.76	25	65	250	30	3.8
W. A. Fox	.84	.70	.80	25	35	250	30	4.0
A. D. Little	.82	.83	.77	25	50	200	25	4.00
A. L. Dean	.82	.80	.81	25	50	200	25	4.20
H. C. Reed	.82	.74	.80	25	65	250	30	4.00
E. W. White	.81	.61	.84	25	40	200	25	4.37
D. L. Tucker	.78	.70	.79	25	30	250	30	3.95
H. T. Wilson	.76	.74	.72	25	60	200	50	7.50
F. M. Loveland	.76	.64	.72	25	60	200	50	7.50
J. V. R. Evans	.74	.72	.76	25	30	250	30	3.80
A. W. Hoppenstedt	.74	.73	.65	50	50	250	30	6.50
W. K. Alsop	.74	.66	.72	25	25	250	30	3.60
Stewart and Veitch	.72	.66	.66	25	..	200	30	4.10
G. M. Trostel	.70	.71	.71	25	40	200	25	3.70
Allen Rogers (C. B. Kinney)	.70	.62	.64	25	40	200	20	2.70
J. H. Delong	.66	.66	.61	25	50	200	25	3.20
T. J. Mosser	.64	.64	.58	12½	12½	200	50	3.00
C. R. Oberfell	.62	.56	.68	12	50	200	50	3.40
W. P. Maxwell	.58	.60	.61	25	75	200	50	6.30
C. W. Norris	.64	.65	.59	25	60	200	50	6.10
Allen Rogers (F. C. Niederhauser)	.54	.62	.67	25	40	200	20	2.80
H. R. Procter (D. H. Law)	.53	.49	.42	25	50	200	30	2.62
F. H. Small	.47	.45	..	..	..	...	..	...
F. W. Alden	.46	.42	.56	25	..	200	25	2.90
J. E. Rhoads	.30	.30	.30	25	50	250	50	2.50
Average	.68	.64	.67					
Highest	.84	.83	.84					
Lowest	.30	.30	.30					

SAMPLE 2

Analyst	Experiment 1 acidity as acetic acid	Experiment 2 acidity as acetic acid	Experiment 3 acidity as acetic acid	Experiment 3 cc. liquor used	Experiment 3 cc. gelatine used	Experiment 3 cc. dilution	Experiment 3 cc. for titration	Experiment 3 cc. N/10 NaOH
A. D. Little	.74	.75	.72	25	50	200	25	3.75
J. V. R. Evans	.72	.78	.74	25	15	250	30	3.70
W. K. Alsop	.70	.76	.72	25	20	250	30	3.60
D. L. Tucker	.68	.70	.71	25	20	250	30	3.55
A. L. Dean	.66	.80	.71	25	123	200	25	3.70
W. A. Fox	.66	.70	.72	25	15	250	30	3.60
H. C. Reed	.64	.66	.68	25	25	250	30	3.40
R. H. Wisdom	.64	.68	.60	25	25	250	30	3.00
C. W. Norris	.64	.62	.61	25	30	200	50	6.40
C. R. Oberfell	.64	.58	.69	48	50	200	50	13.80
E. W. White	.62	.64	.69	25	35	200	25	3.61
A. W. Hoppenstedt	.60	.58	.52	50	20	250	30	5.20
G. M. Trostel	.58	.56	.65	25	35	200	25	3.40
T. J. Mosser	.58	.58	.49	25	13	200	50	5.10
Stewart and Veitch	.54	.48	.54	25	..	200	30	3.40
H. T. Wilson	.52	.54	.54	25	40	200	50	5.70
F. M. Loveland	.50	.54	.53	25	40	200	50	5.50
W. P. Maxwell	.52	.52	.54	25	50	200	50	5.60
H. R. Procter (D. H. Law)	.45	.48	.38	40	40	200	40	5.06
Allen Rogers (C. B. Kinney)	.38	.42	.43	25	45	200	20	1.80
Allen Rogers (F. C. Niederhauser)	.36	.42	.44	25	45	200	20	1.85
F. H. Small	.35	.35	..	..	..	...	..	...
F. W. Alden	.32	.38	.65	25	..	200	25	3.40
J. H. DeLong	.28	.24	.33	25	50	200	25	1.70
J. E. Rhoads	.26	.26	.24	25	50	250	50	2.00
Average	.54	.56	.58					
Highest	.74	.80	.74					
Lowest	.26	.24	.24					

SAMPLE 3.

Analyst	Experiment 1 acidity as acetic acid	Experiment 2 acidity as acetic acid	Experiment 3 acidity as acetic acid	Experiment 3 cc. liquor used	Experiment 3 cc. gelatine used	Experiment 3 cc. dilution	Experiment 3 cc. for titration	Experiment 3 cc. N/10 NaOH
G. M. Trostel	1.32	1.32	1.30	25	35	200	25	6.80
E. W. White	1.24	1.17	1.27	25	15	200	25	6.60
F. H. Small	1.23	1.23	. ..	..	..	..	..	. ..
A. D. Little	1.23	1.24	1.22	25	50	200	25	6.35
A. L. Dean	1.22	1.18	1.28	25	8	200	25	6.70
W. A. Fox	1.22	1.18	1.20	25	35	250	30	6.00
Allen Rogers (F. C. Niederhauser)	1.22	1.18	1.10	25	35	200	20	4.60
J. V. R. Evans	1.20	1.18	1.20	25	35	250	30	6.00
D. L. Tucker	1.20	1.10	1.18	25	20	250	30	5.90
J. E. Rhoads	1.18	1.18	1.18	25	60	250	50	9.80
H. R. Procter (D. H. Law)	1.17	1.10	.96	15	40	200	50	6.04
Allen Rogers (C. B. Kinney)	1.16	1.17	1.13	25	35	200	20	4.70
C. R. Oberfell	1.16	1.14	1.18	12	50	200	50	5 90
F. W. Alden	1.16	1.02	1.23	25	..	200	25	6.40
J. H. DeLong	1.14	1.14	1.21	25	50	200	25	6.30
H. C. Reed	1.14	1.12	1.16	25	35	250	30	5.80
R. H. Wisdom	1.14	1.12	1.16	25	35	250	30	5.80
H. T. Wilson	1.14	1.12	1.10	25	60	200	50	11.50
A. W. Hoppenstedt	1.13	1.08	1.13	50	40	250	30	11.30
W. K. Alsop	1.12	1.08	1.18	25	25	250	30	5.90
F. M. Loveland	1.12	1.10	1.09	25	60	200	50	11.40
T. J. Mosser	1.12	1.08	1.06	12½	17½	200	50	5.50
Stewart and Veitch	1.12	1.12	1.15	25	..	200	30	7.20
C. W. Norris	1.08	1.07	1.07	25	25	200	50	11.15
W. P. Maxwell	1.08	1.02	1.06	25	100	200	50	11.00
Average	1.17	1.14	1.16					
Highest	1.32	1.32	1.30					
Lowest	1.08	1.02	.96					

SAMPLE 4.

Analyst	Experiment 1 acidity as acetic acid	Experiment 2 acidity as acetic acid	Experiment 3 acidity as acetic acid	Experiment 3 cc. liquor used	Experiment 3 cc. gelatine used	Experiment 3 cc. dilution	Experiment 3 cc. for titration	Experiment 3 cc. N/10 NaOH
G. M. Trostel	1.14	1.12	1.29	25	35	200	25	6.70
A. L. Dean	1.12	1.08	1.17	25	18	200	25	6.10
A. D. Little	1.12	1.12	1.11	25	40	200	25	5.75
J. V. R. Evans	1.12	1.04	1.14	25	15	250	30	5.70
J. H. DeLong	1.08	1.04	1.11	25	50	200	25	5.80
R. H. Wisdom	1.08	1.04	1.10	25	30	250	30	5.50
W. A. Fox	1.08	1.04	1.10	25	25	250	30	5.50
J. E. Rhoads	1.08	1.08	1.09	20	50	200	50	9.10
C. R. Oberfell	1.06	1.04	1.09	24	50	200	50	10.90
H. C. Reed	1.06	1.04	1.08	25	30	250	30	5.40
Stewart and Veitch	1.06	1.04	1.08	25	..	200	30	6.70
F. H. Small	1.05	1.05	. ..	..	..	...	..	. ..
W. K. Alsop	1.04	1.03	1.06	25	25	250	30	5.30
Allen Rogers (C. B. Kinney)	1.04	1.02	1.03	25	25	200	20	4.30
D. L. Tucker	1.04	1.00	1.04	25	20	250	30	5.20
F. M. Loveland	1.04	1.00	1.02	25	50	200	50	10.60
H. T. Wilson	1.04	1.02	1.02	25	50	200	50	10.70
H. R. Procter (D. H. Law)	1.04	1.00	1.01	30	40	200	25	6.33
A. W. Hoppenstedt	1.04	.97	1.06	50	30	250	30	10.60
Allen Rogers (F. C. Niederhauser)	1.02	1.04	1.10	25	25	200	20	4.60
E. W. White	1.00	1.02	1.13	25	12	200	25	5.96
T. J. Mosser	1.00	1.02	1.04	12½	12½	200	50	5.20
W. P. Maxwell	1.00	1.02	1.01	25	75	200	50	10.50
C. W. Norris	1.00	.98	1.02	25	45	200	50	10.20
F. W. Alden	.96	.92	1.02	25	..	200	25	5.30
Average	1.05	1.03	1.08					
Highest	1.14	1.12	1.29					
Lowest	.96	.92	1.01					

SAMPLE 5.

Analyst	Experiment 1 acidity as acetic acid	Experiment 2 acidity as acetic acid	Experiment 3 acidity as acetic acid	Experiment 3 cc. liquor used	Experiment 3 cc. gelatine used	Experiment 3 cc. dilution	Experiment 3 cc. for titration	Experiment 3 cc. N/10 NaOH
G. M. Trostel	.80	.72	.80	25	10	200	25	4.20
A. D. Little	.72	.71	.70	25	30	200	25	3.65
J. V. R. Evans	.70	.62	.66	25	5	250	30	3.30
A. L. Dean	.66	.70	.65	25	70	200	25	3.40
J. E. Rhoads	.64	.64	.65	25	30	150	50	9.00
C. R. Oberfell	.64	.62	.67	48	50	200	50	13.30
F. H. Small	.63	.67	...	.	..	...	..	. ..
J. H. DeLong	.62	.66	.69	25	50	200	25	3.60
W. A. Fox	.62	.62	.62	25	8	250	30	3.10
W. K. Alsop	.62	.62	.62	25	10	250	30	3.10
D. L. Tucker	.62	.60	.60	25	10	250	30	3.00
F. M. Loveland	.62	.60	.58	25	25	200	50	6.10
H. C. Reed	.60	.60	.64	25	15	250	30	3.20
R. H. Wisdom	.60	.60	.66	25	15	250	30	3.30
H. T. Wilson	.60	.62	.60	25	25	200	50	6.30
A. W. Hoppenstedt	.60	.59	.60	50	10	250	30	6.00
T. J. Mosser	.60	.60	.56	25	10	200	50	5.80
Stewart and Veitch	.60	.58	.58	25	..	200	30	3.60
F. W. Alden	.60	.58	.71	25	..	200	25	3.70
E. W. White	.58	.62	.65	25	10	200	25	3.45
H. R. Procter (D. H. Law)	.58	.59	.55	50	50	200	50	11.80
Allen Rogers (C. B. Kinney)	.56	.56	.60	25	75	200	20	2.50
Allen Rogers (F. C. Niederhauser)	.56	.56	.57	25	75	200	20	2.40
W. P. Maxwell	.56	.56	.56	50	75	200	50	11.70
C. W. Norris	.56	.55	.55	25	20	200	50	5.75
Average	.62	.615	.63					
Highest	.80	.72	.80					
Lowest	.56	.55	.55					

SAMPLE 6.

Analyst	Experiment 1 acidity as acetic acid	Experiment 2 acidity as acetic acid	Experiment 3					
			acidity as acetic acid	cc. liquor used	cc. gelatine used	cc. dilution	cc. for titration	cc. N/10 NaOH
J. V. R. Evans	.20	.20	.16	25	10	250	30	.80
A. D. Little	.20	.19	.17	50	20	200	25	1.80
G. M. Trostel	.18	.16	.21	25	15	200	25	1.10
W. K. Alsop	.17	.17	.16	50	10	250	30	1.60
J. E. Rhoads	.16	.16	.15	25	30	150	50	2.10
H. T. Wilson	.15	.16	.18	25	15	200	50	1.90
E. W. White	.15	.12	.13	25	10	200	25	.70
A. L. Dean	.14	.22	.15	25	8	200	25	.80
F. M. Loveland	.14	.14	.13	25	15	200	50	1.40
D. L. Tucker	.14	.14	.12	25	20	250	30	.60
W. A. Fox	.14	.12	.14	25	10	250	30	.70
Stewart and Veitch	.14	.14	.14	25	..	200	30	.90
C. R. Oberfell	.13	.12	.14	48	50	200	50	2.70
R. H. Wisdom	.12	.12	.12	25	15	250	30	.6
H. C. Reed	.12	.12	.12	25	15	250	30	.60
W. P. Maxwell	.12	.12	.12	50	75	200	50	2.40
J. H. DeLong	.12	.10	.13	25	50	200	25	.70
T. J. Mosser	.11	.12	.12	25	5	200	50	1.30
F. H. Small	.11	.11	..	..	..	...	..	...
A. W. Hoppenstedt	.10	.11	.12	50	10	250	30	1.20
do.	..	..	.11	5	none	...	..	.95
do.	..	..	.12	10	none	...	..	2.00
Allen Rogers (F. C. Niederhauser)	.10	.10	.12	25	75	200	20	.50
Allen Rogers (C. B. Kinney)	.10	.10	.096	25	75	200	20	.40
F. W. Alden	.10	.08	.13	25	..	200	25	.70
C. W. Norris	.10	.10	.10	25	10	200	50	1.10
H. R. Procter (D. H. Law)	.096	.096	.084	50	25	200	50	1.80
Average	.135	.133	.134					
Highest	.20	.20	.21					
Lowest	.096	.08	.084					

A number of collaborators sent comments or opinions of the method and such extracts from these as may be of interest are given:—

ARTHUR D. LITTLE: "The results obtained are taken from four titrations on each sample for each experiment and the average number of cc. of N/10 NaOH is given.

The three methods appear to give consistent results, but we experienced more ease of manipulation and titration with the water gelatine method than with the two alcoholic ones. The precipitate settles more rapidly and appears to clarify the solution more thoroughly than did the precipitate in the alcoholic solution. The resulting liquid was much lighter in color and the end point in the titration was more easily seen.

We note that Mr. Reed states that a loss of acid occurs when a water gelatine solution is used, but this was not apparent in our experiments.

The use of Hematin as an indicator is the one difficulty in the method and the detection of the end point requires a great deal of practice. We were unable to detect the true end point until a practice run had been made on each sample. The titrations were carried out in porcelain dishes which facilitated the detection of the change a great deal.

Samples No. 1 and No. 2 gave a dark turbid solution and the precipitate settled very slowly. The end points were in the bluish purple. We had the most difficulty with these two samples.

Samples No. 3 and No. 4 gave a light yellow solution fairly clear and the end points were toward the reddish purple.

Samples No. 5 and No. 6 settled rapidly and gave slightly colored solutions. These two had a very distinctive end point, No. 5 being in the red wine color and No. 6 in the red purple.

On the whole, we think the method satisfactory especially where the determination of "acidity of liquors" is routine work. If the method is to be used for a few determinations by an analyst who is not familiar with the method, he should acquaint himself with the end point in order to insure success and accuracy in his work."

C. W. NORRIS: "In carrying out these experiments, I find that the precipitates due to the water solution of gelatine settle more

quickly and the supernatant liquor contains less coloring matter.

I find, as the end point of the titration is approached the solution passes through various shades of color; also that all tanning materials do not give the same color; so it is difficult to obtain the same end point each time. Only by considerable practice in titrating tannery liquors can one expect to obtain uniform results.

I have not observed any advantage of the alcoholic gelatine over the water solution of gelatine."

F. W. ALDEN states that he had difficulty in detecting the end points when titrating; also that his results for Experiment No. 3 would have been lower if the same dilution of the detannized liquor had been used as in the other cases as he found such to be the case by experiment.

H. C. REED AND R. H. WISDOM: "Experiment No. 3 was carried out according to the method now being followed in this laboratory, *i. e.*, 25 cc. of the liquor was pipetted into a 250 cc. flask the requisite amount of alcoholic gelatine added and the whole made up to 250 cc., well mixed and then thrown on a filter, to which had been previously added a small amount of kaolin. 30 cc. of the filtered solution was then used for titration. We noticed that the solutions before titration in Experiment No. 2 were less colored than those obtained by experiment No 1.

The gelatine furnished gave an alkaline solution which made it necessary to neutralize with acetic acid. In this connection it was noticed that after neutralization with acetic acid, the alkaline solution was colored first pink, and then upon addition of two or three more drops of alkali, blue.

C. R. OBERFELL: "I have been using the gelatine method about six months and I have no reason to condemn it. It serves admirably on our class of liquors. I think the end reaction is a little more distinct in the alcohol solution and noticed it most on the hemlock liquors.

The higher values by experiment No. 3 I attribute to the greater dilution of the titrated solution, which was 200 cc. Water gelatine solution gives uniformly low results, perhaps due to absorption of a small quantity of acid.

The alcoholic-gelatine solution is very prone to jellify and I

have found that if less alcohol is used this condition is overcome to a certain extent without sacrificing accuracy."

T. J. MOSSER states that the samples were much more difficult to titrate than any liquors that he has to test, especially No. 1 and No. 2.

E. W. WHITE: "Experiment No. 1 seems to be the best method."

H. T. WILSON: "Some of the end points were very difficult for me to get. With a great deal of experience I think that the method would be a very good one. With some of the samples there were two or three distinct changes of color which made it partly guess work with my limited experience."

A. L. DEAN: Remarks on the difficulty of determining the exact end point and the fact that color changes are not always the same. In some cases being from red to blue and with others the change is to red and the addition of more alkali producing only a deeper red.

He prefers the alcoholic solution of gelatine and the method given under experiment No. 1, where a fixed amount of gelatine is specified.

J. H. DELONG states that he prefers the third method using more dilute solution than specified in the others. Under these conditions he finds the end points more certain.

G. M. TROSTEL: "I found it somewhat difficult to judge the end point of the titration, as I have never used hematin as an indicator. I found more difficulty with some samples than others.

I think that the water solution gave better precipitates than the alcoholic gelatine solution. Number 2 experiment would be very easily conducted and more easily titrated if the volume for titration should be filtered instead of being allowed to settle, as it is easier to judge the end point in a clear solution than a muddy one."

F. P. VEITCH: "You will note that the results differ considerably when the titrations were made to the full color rather than the first tinge of blue. While it is quite difficult for the inexperienced to see the end point, I believe that with practice this can be distinguished quite sharply.

As neither Mr. Stewart nor myself had had previous experience with the methods, our results may differ somewhat from those obtained by more experienced workers.

One other comment in regard to this work is, that I believe accuracy would be increased by taking larger quantities for titrations. It seems to me that in all of these liquors 50 cc. might as well have been diluted to 250 cc. and 60 cc. of the diluted liquor used for titrations. The titration error would thus have been, probably, much lower."

Their results showing differences in titrations are as follows:—

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
First change	.72	.54	1.12	1.06	.60	.14
Full color.....	.90	.58	1.32	1.14	.72	.24

Dr. Allen Rogers states that after a few experiments he had all of the solutions filtered as better titrations were obtained by so doing.

F. H. SMALL: "With regard to ease of manipulation there is little choice between the methods. At least on the sample submitted and on the samples of liquors used in the tannery here there seems to be no need of attempting to proportion the gelatime to the tannin content of the liquor. In all cases a well defined curdy precipitate was formed which settled rapidly. The supernatant liquor was clearest when the water gelatine solution was used. Inasmuch as methods 1 and 2 call for uniform practice they would seem to show some slight advantage over method 3.

With regard to the end point, it undoubtedly requires some considerable practice to familiarize oneself with the various color changes of the hematin in the different liquors. The hematin passes through a rather wide range of tints and there is no sharp well defined end point. Nevertheless there is a point of most rapid change where the tint alters most rapidly, which is fairly readily observed and which can be duplicated on the whole rather surprisingly well. With regard to accuracy, there seems comparatively little choice. It is perhaps true that the color changes of the hematin are sharper and more easily observed when the alcoholic gelatine is used. Any method which estimates an apparent acidity, whose results are not dependent on a particular quality of some reagent which may be difficult of dupli-

cation, which is easy and rapid of execution, and here is the essential point—will give the same result on the same liquor time after time, is a satisfactory method for our Association to adopt. It will enable any chemist to tell whether the liquor in the tannery which he is watching alters in this particular characteristic and if so, whether up or down—that is the only essential. No acid method will enable us to make a comparison of the relative plumping effect of two liquors from two different yards.

Method No. 2 seems to me to answer the above requirements sufficiently well and I am in favor of its adoption as the official method of the Association."

These samples were not picked out with the object of obtaining a closely agreeing set of results from the collaborators but in order to thoroughly test the method and to obtain opinions as to its practicability and worth. Samples Nos. 1 and 2 are the most difficult liquors in which to determine acid by this method of any with which I am familiar. This also applies to most other methods. Sample No. 3 is also difficult, there being practically two end points in the tiration.

The results as a whole are fully as good as I expected to receive and when the difficulties of the titrations and the fact that fully one-half of those sending in results had little or no experience with the method are taken into consideration, I consider that the results on samples No. 3 No. 4 and No. 5 are good and probably agree more closely than would be the case if tested by any of the methods in use, or perhaps it would be better to say: agree as well and show more nearly the actual acidity than by other methods.

I tested my set of samples two months after sending the others out and could not detect any change in the acidity, or manner of titrating, in the case of samples Nos. 3, 4, 5 and 6.

Samples Nos. 1 and 2 did seem to act somewhat differently in respect to the titration, giving somewhat lower results than were obtained at first. The amount of acid present seemed, however, to be practically the same. Upon precipitating with gelatine as in experiment No. 2 filtering and titrating with

phenolphthalein the acidity in No. 1 was found to be .88 per cent. and No. 2 .81 per cent.

They were also tested in another manner; after precipitating with the gelatine and filtering, sufficient amounts of N/10 NaOH were added to definite volumes of the solution to neutralize varying quantities of acid. The solution was then distilled and the distillate tested for acidity.

Under these conditions, the distillate from No. 1 sample was acid when sufficient alkali had been added to neutralize .85 per cent. and neutral at .95 per cent. acid; indicating that the acidity was about .90. Similar tests with No. 2 sample showed acid at .75 per cent. and neutral at .85 per cent. acid.

Precipitation with gelatine under the conditions of these experiments and titration with phenolphthalein is the best method for liquors of this character that I know of. This method, however, fails entirely with liquors such as Nos. 3, 4, 5, and is very poor with No. 6.

Experiments show that the amount of acid found in Nos. 1 and 2 depend very considerably upon the speed of titration and the amount of liquor titrated; dilute solutions and ripid titration giving the highest acidity.

The method cannot be said to work very well with this kind of liquors, which are pure hemlock bark liquors and comparatively rarely encountered, however, comparative results can be obtained and also the actual amount of acidity indicated with reasonable accuracy.

I make no recommendation for or against the adoption of this method by the Association as the replies from the collaborators do not warrant me in so doing. I know of no method that will apply equally well to all classes of liquors and believe this one to be a better routine method for a greater variety of liquors than any other.

Either the alcoholic or water solution of gelatine answer sufficiently well for precipitation when used under proper conditions and what is needed is a better indicator than hematin, which like it, is not affected to any considerable extent by the presence of tannin in the solutions to be titrated.

COLLOIDS AND THE ULTRA MICROSCOPE.

By A. A. Claflin.

To physicists for some time familiar, the importance and value of Professor R. Zsigmondy's work with the ultra-microscope, in the solution of problems in technical chemistry has been somewhat generally overlooked. The appearance of the English translation by Jerome Alexander of "Zur Erkenntniss der Kolloide" under the more apt title of "Colloids and the Ultra-Microscope" will undoubtedly have a popularizing effect and widen the scope of ultra-microscopic research. Many writers in the field of leather chemistry will view Zsigmondy's work almost as a revelation, making as it does an optical demonstration concerning the correctness of some heretofore very debatable hypotheses. The talks and papers which Mr. Alexander, the translator, has given the past season, concerning his own work along the lines of Zsigmondy's research, have still further increased interest in this most attractive subject.

There is scarcely a phenomenon in nature more common than the visibility of ordinarily unseen floating specks in a bright sunbeam. Faraday applied this same principle to test the homogeneity of what we now call colloidal gold solutions, by passing through them the suns rays condensed by a burning glass. The luminosity of particles of matter in sufficiently strong light was further developed by Tyndall, and was made of technical use fairly recently in testing the purity of gases for the contact sulphuric acid process. Zsigmondy by a combination of condensing lenses and reflecting prisms attached to an ordinary microscope applies the principle of magnification to the contents of the light beam. This meagre description of course does not do full justice to the beautiful instrument devised by Zsigmondy, and his able co-worker H. Seidentopf, but it shows the essence. By this ultra-microscope the range of the ordinary microscope is increased seven hundred times, that is, particles which have no greater size than that calculated for a large molecule, become sufficiently luminous to be seen. To live to actually see a molecule was frankly beyond the expectation of your reviewer.

It was indirectly that the value of the ultra-microscope in

colloidal chemistry became apparent in that in this field the results were particularly striking. Colloids are lethargic solutions because their molecules are big, and by the help of this new instrument these lazy ones can be seen. Just what bearing this will have on the manufacture of leather will require much thought, but in its elements the principles of tanning is contained in "Colloids and the Ultra-microscope." Tannic acid is the reversible and the hide substance the irreversible colloid, their mutual attraction the operation of tanning.

The going back to the never-surpassed experimental work of Faraday, and the original papers of Graham adds much interest to the book.

It is, of course, easy to predict too much for ultra-microscopy. Zsigmondy modestly declares that is is one more method added to those already known for physical chemistry research. In the opinion of the reviewer it is more, it is a considerable step in the direction of effacing the line of separation between physics and chemistry. To all students of the principles of tanning "Colloids and the Ultra-Microscope" is most heartily recommended.

RECENT ADVANCES OF THE CHEMISTRY OF THE TANNINS.[1]

By Dr. M. Nierenstein.

Comparatively few other products have been subjected to the careful investigation of well-known scientists, as the tannins. Amongst the many workers in this field of research who may be mentioned are such men of world-wide repute in the scientific world, as Scheele, Liebig, Berzelius, Humphrey Davy and Perkin. Our knowledge of this particular branch of organic chemistry is however very far from being complete.

It is not my intention to deplore the unsatisfactory state of our knowledge, nor do I mean to discuss in detail the progress which has been recently made in the direction of the isolation of the particular tannins; it will suffice if I mention a few of the later achievements in this direction, with the endeavor of pro-

[1]From *Leather.*

moting some amount of interest in a subject which is likely to have a very far reaching effect in the future, and become a matter of extreme importance to the tanner.

The chemistry of the tannins is, as above stated, very imperfectly understood and is so complex that an account of the present position written in chemical phraseology would be of no interest to the average leather trade reader who possesses little knowledge of chemistry.

To many readers a study of such a subject may seem of very minor importance indeed, and as a matter of fact I have been asked the question very many times: What is the use of knowing the chemical constitution of tannin, and how will this knowledge help the leather manufacturer?

Though this question is a very difficult one to answer at the present moment, a comparison with other industries which have been completely revolutionized by the scientist devoting his attention to the chemistry of natural products shows how the tanning operation might be affected once the chemistry of tannins were better understood.

A striking example of the very far reaching effect that chemical science has had, and the tangible benefit which has been derived by mankind through the devotion of scientists to the investigation of indigo and alizarine; both of these valuable dyestuffs are now being manufactured from coal tar products and are the direct outcome of the result of investigations into the constitution of the natural dyestuffs, which they have to all practical purposes entirely supplanted in the commercial world.

Many attempts have been made to classify and group together the various tannins, but until our knowledge of the chemical constitution of these very varied products of nature is more complete, it is only possible at the present time to make a classification which is entirely based on their chemical and technical known properties. One classification, namely that obtained by employing bromine water as suggested by Professor Procter, as a reagent, is based on the above conditions. I have adopted this classification as the base of my work in the investigations of tannins.

The pyrogallol tannins are noted for their "bloom-giving" properties. Researches made in the investigations of the bloom deposited have conclusively proved that the bloom deposited by solutions of bark; the "bloom" deposited by solutions of fruit, e.g., myrabolams, valonea, etc., and the "bloom" recovered from the surface of a tanned skin, consists of Ellagic acid.

Ellagic acid has recently been produced synthetically from gallic and tannic acids, and as its constitution has now been satisfactorily proved, it has thrown some little light upon the chemistry of tannic acid.

Without going into chemical detail it might be of interest to state that tannic acid apparently consists of two products, one of them being digallic acid and the other Lueco-tannic acid. This fact throws some light on the manner of bloom formation, presuming that the tannic acid—the digallic acid—is oxidized by the plant and precipitated in the bark. This is explained by the fact that presence of Luteoic acid (the intermediate oxidation product of tannic and ellagic acid) has been discovered by me in myrabolams. It has also been synthetically produced by oxidizing tannic acid with hydrogen peroxide.

The pyrocatechol tannins, so well-known by the fact that they deposit "reds," or to give them their scientific term, phlobaphenes, have not been investigated up to the present with any degree of success. The phlobaphenes (or "reds") are well-known as being common to such tannin materials as quebracho, hemlock, etc.—"the difficult soluble reds." The phlobaphenes have up to the present been regarded as the anhydrides of certain tannic acids.

A careful examination of this question by the author has resulted in proving that the pyrocatechol tannins, like the pyrogallol (or bloom-giving tannins) undergo oxidation, and form products which are either of the anthrachinone or the purpurogallin type; and the conclusion is drawn from the investigation that a phlobaphene formation in such plants as the mangrove, is due to an abnormal metabolism; the plant being exposed to many changes, such as water supply, heat, etc.

Pyrocatechol tannins are quantitatively oxidized to phlobaphenes. This is interesting from a technical and practical point

of view, as it shows how undesirable it is to expose to the air solutions of tannins such as mangrove, quebracho, etc., for a long period, particularly when the solution is frequently stirred and mixed with the atmosphere, as, for example, when tanning basils in paddles.

Reference has frequently been made of a third group of tannins; a group which give a reaction with ferric chloride, producing a bluish green color, and give only slight precipitates with bromine water. These have some insoluble "reds" (phlobaphenes) and deposit some slight amount of bloom; these tannins have been generally supposed to be a separate group.

From the results recently obtained by Professor Zellner, who showed that various fungi had a selective liking either for pyrogallol or pyrocatechol tannins, and demonstrated that while *polyporus iginiarius* extracts the one tannin from oak bark, *polyporus velutinus* imbibates the other one. I am inclined to the belief that this third group of tannins, of which oak-bark is an example, is really only a mixture of the pyrogallol and pyrocatechol tannins.

In my own experience I have found that the fungi growing on various tannin solutions have the effect of oxidizing both pyrogallol and pyrocatechol tannins and destroying them entirely.

Considerable danger therefore exists by the growth of fungi on the surface of tan liquors in actual use, and same should be avoided by the addition of some small quantity of a germicide to the liquor itself.

THE EMPLOYMENT OF FORMIC ACID IN TANNING.[1]

The following information on the utilization of formic acid in tanning is based on the outcome of practical experience in France, and the points summarized are, we think, well worth bearing in mind, even if modifications have to be made to suit other methods in this country.

The goods on removal from the lime-pit are fleshed, unhaired. and scudded as usual.

At the last scudding, rather more carefully carried out to

[1] From *The Leather Trades Review*.

insure the removal of the short hair, the hides are removed to a cemented or wooden vat containing:—3 lbs. formic acid 90 per cent., to 1,000 lbs. clear hide, and a sufficient quantity of water to steep the hides.

The suspension of the hides from the sides or from rods is always better than piling them up in the vats.

By suspension, the external surfaces of the hides are more completely flushed with the acid liquor, which dissolves out the lime; when piled one on the other the hides often adhere to each other, and patches thus form which are not completely de-limed. Although by turning the hides three or four times it is possible to partially prevent this inconvenience, it can only be entirely avoided if the hides are suspended.

The hides the then steeped in the bath for 36 to 48 hours, and may be left even longer if desired without injury. A perfect de-liming of the grain is effected more easily by prolonging the steeping than by increasing the quantity of acid.

The same bath may be used two or three times; it is only necessary to make up the strength each time to 3 lbs. 90 per cent. formic acid for each 1,000 lbs. hide weight.

The formic acid possesses no action on the coriin and the gelatine of the leather; they are not dissolved. Its antiseptic action also protects the delimed skins from the moulds of *aspergillus niger* and *penicillin glaucus*. This antiseptic action also allows the repeated use of the deliming bath.

The hides when completely delimed are conveyed directly into the first tanning pit.

Antisepsis can be maintained in the first liquor, and plumping facilitated by adding 100 grams (4 ozs.) of 90 per cent. formic acid to 1 cubic metre (220 gallons) of ooze. In the second and third liquors 50 grams (2 ozs.) of 90 per cent. formic acid per cubic metre (220 gallons) of ooze is added. This prevents putrefaction and promotes plumping.

In the fourth liquor, which is concentrated, the addition of formic acid is discontinued, as well as in the fifth and sixth liquors. In the stronger oozes neither antisepsis nor plumping is necessary. Formic acid, if added to strong tanning solutions, causes the leather to plump too much, and whatever the means

employed, every time leather is too much plumped a brittle product is produced.

Formic acid does not render leather brittle, but if the hides are plumped too much, it does not prevent the leather from becoming brittle.

As already mentioned, formic acid does not attack the leather at all. It is a powerful antiseptic, and used in the tannery after deliming, without exceeding the quantities above given, it has, as a result of several years' technical experience, given much satisfaction in many large tanneries.

ABSTRACTS.

The Relation Between Tanning and Science During the Last Half Century. F. H. HAENLEIN. *Jahresber Deutsch. Gerberschule,* 1908-9.—This is essentially a classified chronological list of the various elements which have contributed to the science of tanning. It cannot well be abstracted, but some extracts are here given.

The methods of tannin determination prior to 1883 are grouped as: (1) hide absorption methods, beginning with Davey's old process employing dried hide, and determining increased weight; later improvements were use of powdered hide, examination of the solution before and after precipitation of tans, by specific gravity determination (Hammer) and by examination of the evaporated residue (Müntz and Ramspacher); (2) precipitation with gelatine solution, compared with a known standard tannin solution (Warington, Fehling), improved by adding salts, alum (G. Müller), sal-ammoniac (Schulze), ferric chloride (Hartig; (3) precipitation by alkaloids, especially cinchonine (R. Wagner, Clark); (4) precipitation with salts of heavy metals, ferrous acetate (Hanchke), copper acetate (Fleck), lead acetate (Prebram, Allen), stannous chloride, tartar emetic, mercuric nitrate, etc.; (5) colorimetric with ferrous salts (Wildenstein); (6) absorption in alkaline solution of oxygen (Mittenzwei, Terreil) or of iodine (Jean, 1876); (7 oxidation methods with iodic acid (Comaille), with bleaching powder (Prudhomme), and particularly with permanganate (improved by Löwenthal 1861, Neubauer 1875, and von Schröder).

In 1883 a congress of tanning chemists at Berlin adopted for unification Löwenthal's method, which prevailed until displaced by the hide absorption methods, developed from 1897 to the present.

After an account of the organizations and educational institutes follows a catalogue of the journals published pertaining to the tanning industry. This we reproduce complete; when not otherwise specified the journal appears weekly.

1858. *"Zeitung für Lederfabrikation und Lederhandel,"* changed 1859

to *"Gerberzeitung"* (Kampffmeyer), changed 1896 to *"Schuhund Leder,"* since then confined to the shoe industry.

1865. *"Deutsche Gerberzeitung"* (Günther), since 1907, six times a week; title changed 1909 to *"Lederindustrie."*

1857. *"Halle aux Cuirs,"* Paris; *"Shoe and Leather Reporter,"* Boston.

1860. *"Gerber Courier,"* Vienna.

1868. *"Leather Trades Circular,"* London; *"Berliner Berichte,"* Berlin.

1874. *"Leder-Interessent,"* Berlin, discontinued 1893; *"Der Gerber,"* Vienna (twice a month).

1875. *"Der Süddentsche Gerber,"* Waldsee, Würtemberg, discontinued 1900.

1876. *"Shoe and Leather Review,"* Chicago.

1878. *"Nordisk Garvertidende,"* Copenhagen, (twice a month).

1879. *"Der Ledermarkt,"* Frankfort on the Main.

1880. *"Schönmann's Journal für Lederindustrie,"* Vienna.

1881. *"The Scottish Leather Trades,"* Glasgow, (monthly).

1882. *"Zentralanzeiger für Deutschland's Lederindustrie,"* Neudamm.

1883. *"Bourse aux Cuirs de Liége,"* Liége.

1886. *"The Shoe and Leather Record,"* London.

1888. *"Allgemeiner Anzeiger für Lederindustrie und Handel,"* Ohligs, Rhine Province, discontinued 1892; *"Lederabeiter,"* Berlin.

1889. *"Oesterreich-ungarisches Lederblatt,"* Vienna, discontinued 1907; *"Marché des Cuirs,"* Paris; *"De Nederlandsche Lederindustrie,"* Dötinchem, Holland.

1890. *"Schweizerische Lederindustrie Zeitung"* (twice a month); *"The Leather Manufacturer,"* Boston and New York, (monthly).

1891. *"Hide and Leather,"* Chicago.

1892. *"Kozeluzske Listy,"* Prague, (twice a month).

1893. *"Nordisk Garfveri-och Läder-Tidning,"* Stockholm, (twice a month); *"La Conceria,"* Turin, changed 1907 to *"La Conceria e Calzoleria,"* Milan, (twice a month).

1884. *Magyar Böripar,"* Budapest, (three times a month).

1899. *"Allgemeine Gerberzeitung,"* Vienna; *"Collegium,"* Frankfort, (scientific supplement to *"Ledermarkt"*).

1903. *"Leipziger Schu- und Lederzeitung,"* Leipzig; *"Timarok Lapja,"* Budapest, changed 1904 to *"Böripari Szemle,"* (twice a month); *"Der Russische Gerber,"* Liban, (twice a month).

1906. *"Häute und Leder,"* Berlin.

1907. *"Leder und Schuhe,"* Warsaw, (twice a month); *"Die Treibriemenindustrie,"* Dresden.

1908. *"Le Cuir,"* Paris, (twice a month); *"Technische Briefe,"* Berlin, (monthly).

1909. *"Ledertechnische Rundschau,"* Berlin, (technical part of *"Lederindustrie"*); *"Leather, Technical and Practical,"* London, (monthly); *"Monitorul Industriei de Piele,"* Bukarest, (twice a month); *"Suomen Nahkurilehti"* (Finnish Tanner's Journal), Helsingfors, (monthly).

Formaldehyde in Tanning. U. J. THUAU. *Le Cuir,* 1909, [2], Nos. 8, 9, pp. 201-8.—Hide fibre after treatment with formaldehyde is not rendered completely insoluble by action of tanning agents. In such a leather, after retanning, the formaldehyde may be extracted and recognized by tests. As tests for formaldehyde, the phloroglucine or fuchsine reactions may be used, but the writer prefers phenyl hydrazine hydrochloride, followed by a few drops of ferric chloride and sulphuric acid; a characteristic red color is produced. The writer has found that cow-hide already completely tanned by formaldehyde, is retanned in a chrome alum bath three times as rapidly as when formaldehyde has not been used, giving a strong leather. On boiling this with water, formaldehyde could be detected. Similar results were obtained on retanning with chestnut extract.

Formaldehyde is also used alone without alkali to fix plumped hides before a rapid tannage in the drum. In this case, if the butts are not well delimed, the lime remaining in the hide polymerizes the aldehyde, giving a compound which tans the hide; the tannage is then vigorous, but gives poor rendement. Complaint is often made of obtaining dark leather after use of formaldehyde. This is due to the use of sulphited extracts; formaldehyde which combines with bisulphite of soda, restores colors. This may be demonstrated by treating with sulphited quebracho, parallel samples of hide which have and have not been fixed with formaldehyde; in the last case, the color will be much lighter. Another application of formaldehyde is in the treatment of furs and hides which are to be tanned without removal of the hair. The grain is thus made firm, and the hair resists withdrawal. The writer suggests the use of formaldehyde for bleaching tanned leather; the loss of tannin is insignificant and the color is much clearer.

Formaldehyde Tannage. A. GAGNARD. (As above). In the discussion following M. Thuau's paper (read at the reunion of the French Section), M. Gagnard also agrees that the formaldehyde treatment promotes a rapid penetration of tanning material. He has completed a tannage in the drum in 30 hours, producing an apparently perfect leather. On storage, however, for a month, the leather lost its firmness and became brittle and hygroscopic. This is due to the oxidation of the aldehyde to formic acid within the pores of the leather. In conclusion, the formaldehyde process is not a real tannage and does not produce genuine leather.

School of The Tanner; Plumping (continued). A. SCHMIDT. *Le Cuir,* 1909, [2], No. 10, pp. 219-21.—Ordinarily, plumping is effected by soaking in old tan-liquors, the result being due to the acids previously produced by fermentation. The objection to the exclusive use of acids from this source is the great variation in amount, due especially to variations in temperature. Moreover, such acid cannot be produced beyond a certain strength when the fermentation is arrested. Good tannage can be effected with such acids, but the process is too slow. In the ancient

process, which largely took care of itself, greater latitude was permissible. The modern, rapid process requires a more precise control, with regular gradation of acids. For this reason, an addition of artificial acids is generally made, especially to the stronger liquors. Another modern device for accelerating the fore-tannage, is the employment in advance of a special bath for plumping. In the succeeding tannage, it is necessary to maintain a proper proportion of acid, even if the hides have been already sufficiently swelled, otherwise, they will fall again in spite of the presence of tannin. For artificial acids, acetic or lactic are best, and recently oxalic and formic acids have been used with success. Sulphuric and hydrochloric acids are much in use, but there is more risk of injury to the leather.

Methods of Making Soft Leather Firmer. *Magyar Böripar,* [16], Nos. 4, 5, through *Collegium,* 1909, No. 357, p. 165.—In the rapid tanning processes of the present day, the hide fibre is generally much loosened in texture in order to bring about a quick absorption of tannin. This produces a soft and spongy leather which can only be improved by afterwards saturating with such tans as render leather firm. This is best done in the drum after the hides from the regular tannage have been drained. Light-colored tan-stuffs are best, such as extracts of oak, chestnut, valonea, etc. A liquor of 8 to 9°B. may be used, during 6 to 12 hours. The leather can also be put in the drum in the dry state and then takes up tans even easier. There is then, however, more risk of a dark-colored and brittle product, which is lessened by thorough washing of the grain, oiling and slowly drying.

A second method of hardening soft sole leather is to thoroughly roll it in the dry state. The stage of dryness is, however, important; the leather should neither be moist nor absolutely dry. With very soft leather, the rolling is best repeated, shortly before drying. Leather may also be improved in firmness by rapid drying; moist leather always feels soft. Most of the salts, glucose and other materials used for weighing are hygroscopic. The only permissible loading material is tannin, which also improves the quality of the leather.

PATENTS.

Leather-Working Machine. U. S. Patent No. 922,195. F. K. RUSSELL, Dallas, Texas. A machine for finishing leather straps.

Skiving Machine. U. S. Patent No. 922,214. J. S. TURNER, Lowell, Mass.

Automatic Hide-Tanning Machine. U. S. Patent No. 922,415. C. J. GLASEL, South Boston, Mass. A tanning drum provided with means for alternate immersing and removing the hides from a tanning solution. and for stretching the hides during the process.

Skiving Machine. U. S. Patent No. 924,657. P. R. GLASS, Boston, Mass.

Leather-Dressing Machine. U. S. Patent No. 924,756. M. FRIED AND R. HARVEY, Providence, R. I.

Leather-Working Machine. U. S. Patent No. 924,873. G. V. ANDERSON, Wilmington, Del.

Spring-Roll for Leather-Splitting Machines. U. S. Patent No. 924,900. J. H. GAY AND W. D. QUIGLEY, Newark, N. J.

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THE UNKNOWN FACTOR IN TANNING.

By Robert W. Griffith.

The tanning industry in its evolution, perhaps more than any other industry, owes its development to intelligent observation rather than to scientific theories.

Chemistry and exact science have developed most industries to a point where they can be almost expressed in algebraical equations, but while it is not to be denied that the tanning industry owes an ever increasing debt to the science of chemistry, yet it must be confessed that the progress which the industry has made, more particularly in chrome tanning, owes its development to a succession of blunders, rather than to a well thought-out scheme to revolutionize the old-fashioned methods of tanning.

Our knowledge of chemistry is not yet sufficiently advanced to explain the attraction between certain mineral bases and a high organic structure like hide fibre which results in the production of leather.

The property of rendering gelatine insoluble, possessed by certain salts, cannot be expressed in a chemical equation, and the discovery of this property, which is the basis of all mineral tanning, resulted from careful observation rather than from theoretical deduction.

The highly complex nature of hide fibre has baffled all attempts to arrive at its constitution, and although we may observe its behavior with definite and known compounds, yet, until its constitution is understood, hide fibre will always remain as the unknown factor in tanning.

For the present, therefore, as in the past, progress in the industry of tanning must depend upon careful and systematic observation. The chemist, from the nature of his training, becomes logically the most competent observer.

While the chemist is regarded to-day as an asset in the tanner's business, it is to be feared that his value is estimated upon his ability to detect adulteration in tanning materials, rather than as a factor in the development of the industry.

Chemists frequently complain that they are not given the opportunity to come into close contact with the various processes in tanning, and their assistance is sought only when something

goes wrong, and the chemist is then assumed to be a master of occult science and another "Daniel come to judgment," whereas the truth is, that the chemist, not having had the opportunity to observe and study the influences which work for good and for evil upon the hide, is totally unable to satisfactorily explain the cause which produces the defect. Until the laboratory can define the constitution of hide substance, the tannery chemist's training ground must be the tannery.

It frequently happens that in the absence of proper observation the most erroneous conclusions are arrived at in the tannery as to the cause producing certain results. The slightest divergence from a set procedure yields its results in the product; hide structure responding to the most delicate treatment and being sensitive to many uncertain influences.

The use of a new material, whether a tanning agent or an accessory to the tanning process, necessitates the adjustment of other materials and processes to it, in order to avoid possible failure and consequent condemnation of the material being tested, when it happens that the cause of a difficulty is the influences set up in an entirely different direction.

Illustrating the value of careful observation, the following instance may be cited, which occurred in a tannery producing belting butts, the tannage being principally extract. It happened with almost persistent regularity that a few butts in each pack had spots on the surface which obstinately refused to take the tan. The beam-house foreman gave it as his opinion that the trouble was caused by improper handling in the tail handlers which caused the butts to "kiss." The yard foreman ventured to say that the difficulty was caused by poor beam-house methods, the spots being caused by grease left on the surface of the hide which prevented the penetration of the tan.

The solution was discovered in an entirely different direction to those suggested. The butts were delimed in an acid bath at about 80° F., with the object of removing the surface lime only, after which they were "grained" on the beam and afterwards went direct to the tail liquors. The butts after deliming were placed in an even pile near the beams, and it was observed that the spots on the butts corresponded in size and shape to the indents in the stone floor on which the beamsters worked.

The pressure of a pile of butts upon those butts at the bottom of the pile caused the latter to take an imprint of the surface upon which they rested. This pressure forced lime from the interior of the hide to the surface and on coming in contact with the air this lime quickly carbonated and became fixed, so that it resisted the penetration of the tan. The spots readily yielded to treatment with a weak acid, and the trouble was avoided subsequently by putting the butts in water immediately after leaving the beam.

That a too strict adherence to chemical rules without sufficient consideration being given to the "unknown factor" may prevent the solution of a problem in tanning, is illustrated in the following interesting case:

A pack of pickled hide splits, intended for chrome tanned "gusset" leather, were required to be fairly soft and pliable, after being tanned and treated in the usual way, dried hard and "bony." An examination showed that the chromium had failed to penetrate through the fibre and in consequence there was a "raw streak" in the centre of the fibre which was the cause of the hardness apparent in the finished leather.

The goods were carefully "soaked back" with water and another attempt made to strike the chromium through by the two bath process. This proved ineffective, and a third attempt to drive the chromium through proved no more successful.

The splits had arrived at the tannery in a pickled condition, from a source unknown, so that the manner of their beamhouse preparation was also unknown, but it was apparent that the root of the trouble lay in the fact that the goods had been taken from the splitting machine and while still full of lime were thrown into a pickle. This resulted in the fixation of the lime as an insoluble sulphate which resisted the penetration of the chromic acid.

Now, acids capable of forming soluble salts with calcium oxide, are weaker than sulphuric acid, and as the latter forms a very insoluble salt with lime, such a salt cannot be broken up by a weaker acid, like lactic acid, which would form a soluble lime salt.

But the possibility of a weak organic acid influencing the fibre should be considered, the idea being that calcium sulphate is inert

and that the fibre has little affinity for it; this could be circumvented by a weak acid like lactic acid, that would cause the fibre to swell slightly and by so doing push aside, as it were, the particles of insoluble calcium sulphate and permit of the penetration of the chromic acid.

Because of its non-injurious effect upon the fibre, and the fact that it is non-volatile, and consequently is assimilated by the fibre, lactic acid accomplished this purpose very satisfactorily.

Before closing these brief observations, the object of which is to call attention to the most vital phase of our industry, which is the necessity of a close study of the raw material with which we have to deal, another case might be mentioned which baffled the attempts of many excellent practical men to solve.

This instant is taken from a sheepskin tannery, and the trouble which had arisen was similar to that first described in the present article; that is, the skins refused to absorb the tan, (which was an extract tannage,) in certain spots, but remained white even after the rest of the skin was thoroughly tanned.

One of the disabilities under which the sheepskin tanner labors is, that he obtains his raw material from the wool puller, who prepares the skins for the tanner and ships them to him in a pickled condition. And "pickle" covers a multitude of sins which the unsuspecting tanner later discovers.

In the present case the spots remained flat and hard and were "raw" through the fibre. The trouble was traced to the pulling room where the skins, after receiving an application of a depilatory (usually a mixture of lime and sodium sulphide), have the wool removed and are thrown into a pile and allowed to remain there until they can be leisurely removed to the lime pits. While lying in the pile in a more or less limed condition, the lime, on portions of the skins, carbonated and became fixed in the grain and on the fibre.

The subsequent process of pickling converted the lime carbonate into a sulphate which with time became thoroughly fixed.

This difficulty was, however, eventually overcome by thoroughly washing the skins to remove as much salt as possible, and then giving a fairly strong application of acid. The removal of the salt is important, as its presence will prevent the swelling of the fibre by the acid, and it is upon this plumping effect that

the subsequent penetration of the tannin depends, and like many other problems in tanning, the solution depends upon bringing some influence to bear upon the "unknown factor."

A RAPID METHOD OF ESTIMATING THE ACIDITY OF HIDE-POWDER.[1]

By Alex. T. Hough.

The present Official Method of the I. A. L. T. C. for estimating tannin is now practically beyond reproach so far as concordance is concerned, as may be perceived by perusing the paper recently published by Professor Procter in the *Collegium* (No. 354, 17.4. 1909), and yet there is room for improvement in the labyrinth of details surrounding the main essentials, and in particular—so far as this paper is concerned—in the estimation of the acidity of the hide-powder.

This point raised some little controversy, particularly between Bennett and Small, who pointed out rather cynically that the end point obtained by using the I. A. L. T. C. method was an extremely indefinite quantity, although the American method could not lay claim to greater accuracy.

Naturally a little experience is necessary to judge the end-point of a titration taking from four to five hours, or even more, but nevertheless in careful, experienced hands the I. A. L. T. C. method is capable of yielding very good results, correct to 0.2 ccm., which is near enough for all practical purposes. The *bête noir* of the process however, is the time taken in the titration, and in proportion, the slow effects of the reagents upon the indicator, owing to slow diffusion through the colloid body.

The method now proposed by the author yields results which are identical with those obtained by the Official method of the I. A. L. T. C. and a moderately sharp reaction is obtained with the indicator in proportion to the time taken in titrating, which averages about two or three minutes.

The method simply consists in weighing out the equivalent of 6.5 grams of dry hide-powder as usual, adding about 100 cc. of boiling distilled water, stirring for two or three minutes until the

[1] From *Collegium*.

hide-powder is thoroughly soaked and partly gelatinized and then titrating while hot with N/10 NaOH, using a liberal amount of phenolphthalein (3-4 cc.) as indicator.

Within limits, the more gelatinization which takes place in the hide-powder the better the reaction, and it is even advantageous sometimes to boil the hide-powder for five minutes or so, which treatment will not alter the results.

In this manner a fairly sharp reaction is obtained and a permanent pink results in a minute or two, the figures yielded being at the same time identical with those yielded by the more tedious Official method.

In conclusion I have to thank Mr. J. T. Terrell for his services in this matter.

A PRELIMINARY NOTE ON A GROUP OF LACTIC ACID BACTERIA NOT PREVIOUSLY DESCRIBED IN AMERICA.[1]

By E. G. Hastings.

Various bacteria forming acid in milk have been described. The organisms most frequently met and which are of the greatest economic importance are those belonging to the group represented by *Streptococcus lacticus* (Kruse) or the *Bact. lactis acidi* of Leichmann. This group is characterized by the small amount of acid which the organisms are able to produce in milk. The milk acted upon by pure cultures rarely shows an acidity exceeding one per cent. The limiting factor is apparently the formation of free lactic acid, the organisms being unable to grow in the presence of free acid. As numerous investigations have shown, the amount of acid produced varies with the composition of the milk. Milks high in casein and ash constituents develop a greater amount of acid under similar conditions than do milks whose casein and ash content is lower, because these substances combine with the acid formed.

Freudenreich, in Switzerland, has described a class of lactic-acid-forming bacteria which are able to produce much greater amounts of acid in milk than the organisms of the *Streptococcus lacticus* group. This group of high acid-forming organisms has been brought into prominence recently by the work of Metchni-

[1] From *Science*.

koff and others on the fermented drink yougurt which is prepared from milk. The organisms found in this type of fermented milk are characterized by the production of large amounts of acid, three per cent. and over, by the high optimum temperature for growth, 42-45° C., by growing only under certain narrow conditions on artificial media, and by their morphology, being large bacilli. In all these the organisms from yougurt agree with those described by Freudenreich.

It has not been thought that such organisms are widely distributed. Indeed some writers have asserted that this type was peculiar to the country to which yougurt is native, Bulgaria. Within the last few months it has been found that organisms whose characteristics are similar to those found by Freudenreich in Swiss cheese and to those found in yougurt are of common occurrence in this country.

If a sample of mixed milk is placed in a tightly stoppered bottle and incubated at 37° C. the acidity rapidly reaches one per cent., due to the growth of *Streptococcus lacticus*. The acidity then continues to increase slowly until at the end of two to three weeks it reaches 2.5 to 3 per cent. The flora at first made up almost wholly of the small diplo-bacilli changes, through the appearance of long slender bacilli, which increase in number with increasing acidity.

In cultural characteristics and in bio-chemical reactions, the organism isolated is apparently of the same group as those of Freudenreich and the bacteria in yougurt.

As far as the writer is aware, this type has not previously been found in this country, although it is of wide distribution, and has been present for years. Milk bottled in 1902 was recently opened, and showed an acidity of over 3 per cent. A detailed study of the distribution and characteristics of the organism is being made.

ABSTRACTS.

Nappa Leather. *Ledertechn. Rundschau*, 1909, Nos. 16, 17, pp. 121, 132. —This leather is made from glacé leather, this being treated with vegetable dyes, which also effect an after-tannage. The hides are therefore first tanned in alum and then receive an after-tannage with vegetable tan-stuffs. The reverse order is not desirable for the alum cannot work

sufficiently on fiber already filled by tannin. Only good clean grained pelts should be used for this leather, as all defects are more pronounced in the finished product than in glacé leather.

Method I.—The hides are well washed and are then treated with the egg paste, in which they remain for 24 hours, and are then grounded in the tanning drum with a solution of 50 gms. bichromate potash to 120 liters of water for 100 hides. After ¾ to 1 hour's milling, the liquor is drawn off and the tanning follows. The tanning liquor is prepared by boiling 8 kg. terra japonica with 200 liters water, cooling and settling for at least 2 days; large quantities can thus be made in advance and improve on standing. Of the dye-liquor, mixed from the decoctions of various dye-woods according to the shade desired, 2 liters to each hide are taken, together with 600 to 700 cc. of the japonica. 40 liters of water of 20° R. and 40 liters of above mixture are put in the drum with the hides and milled for 20 minutes, when 40 liters are drawn off and replaced by 40 liters of fresh liquor; this is repeated 5 times. The hides after rinsing and draining are next drummed with 200 gms. of Marseille soap in 40 liters of water, ½ to 1 hour, then piled, lightly stroked, and dried.

Method II.—Lean hides after being well washed are filled as follows: For each hide an emulsion is made of an entire egg with a cooled solution of 5 gms. Marseille soap in 100 cc. of distilled or boiled water, 50 cc. more of water being stirred in. The hides are milled in this for ½ hour, then laid smooth and let lie for 12 hours. For the chrome bath, 100 gms. yellow chromate and 100 liters of water are taken. 2 liters of dye liquor per hide with 0.8 to 1 liter of japonica solution 1:20 (instead of 0.8:20) are used. The after-tannage is extended to 6 hours, as it is important that very dilute solutions be used, and these tan slowly. In beginning, for 100 hides, 55 liters water and only 25 liters mixed liquor are used; 25 liters are drawn off and replaced every half hour. If strong liquors be used and the time shortened only the surface of the hide gets tanned. In order to secure the precise shade desired, which is almost impossible in this drum process, the hides afterward receive a finish dyeing with basic aniline colors. The hides are finally oiled on the grain with bone or olive oil, using a sponge. If the leather is not tanned through, the fat is not absorbed and after drying leaves grease spots. For full hides, well tanned, the treatment is somewhat different. After the usual washing in two waters, they are grounded with bichromate and then tanned and dyed as above. Then follows ½ hour milling with an emulsion of 1 egg yolk, 10 gms. neatsfoot oil and 100 cc. of water to each hide.

Nappa can also be dyed light on the flesh side and the darker shade desired for the grain applied afterwards on the table. In this case, the grounding with chromate is omitted. For very light shades, no dye liquor need be added to the tanning bath, which is made from myrabolams extract instead of japonica, 15 kilos to 200 liters of water. This is diluted with an equal amount of water or dye liquor and the tannage is begun with 25 liters of the mixture and 55 liters of water, replacing 25 liters every half hour.

Brown Dyes.—The different shades count by the hundred and may be considered as compounded of the three simple colors, yellow, red and blue; the mixture being characterized by the one which predominates or in the main, as light, medium and dark browns, corresponding to above. The shade is dependent not only on the ratios of these simple colors, but is also modified or subdued by certain ground or foundation dyes (Grundfarben) as well as dilution by water. These ground dyes include—(1) Pine bark, giving a light brown, covering well. (2) Alder bark, giving a duller, paler shade. (3) Bablah (neb-neb), a ground for brown, is very astringent and in unsuitable proportions gives coarse colors and grain; it is also very useful for grays. The decoction should be filled in closed vessels and let clear a long time. (4) Willow bark, gives very tender, soft shades. As elementary dyes, for producing the composite browns, are used: (1) Fiset wood (Albanian fustic) as yellow element; it produces intense yellow brown shades of unpleasing hue and is tempered with fustic which gives milder shades. (2) Brazil wood (shavings), red element. (3) Logwood and indigo carmine, blue elements. (4) Aniline dyes may be used to intensify the bright shades and various berry juices for deadening and browning the yellow and red dyes. The shading and deepening of the browns are effected by mineral precipitates. These "darkeners" (tourners) comprise: (1) Alum, refined, for light browns; it makes the color clear, and gives the grain a lustre. (2) Zinc sulphate, for intensifying reddish colors. (3) Copper sulphate, for bluish tones. (4) Copper sulphate and iron acetate, dark browns. (5) Salzburg vitriol (copper and iron sulphate mixture), more pronounced dark shade. (6) Iron acetate, darkest. (7) The mordant has considerable influence on the tint of brown. Any addition to the wine mordant of substances which make the color bluer, such as alkali, chromates, sal-ammoniac, etc., must be avoided, but rather such as redden the shade, *e. g.*, tartaric acid, tin and zinc salts.

RECIPES (liters).

	Light brown	Middle brown	Dark brown
Alderbark	4	...	...
Fiset	2	4	2
Fustic	2	2	1
Quercitron	...	...	1
Brazil wood	¾	1½	1½
Logwood	¼	½	¾
Bablah	...	2	...
Indigo-carmine	...	...	½

The dye-wood or bark is extracted with 40 liters water to the kilo; mordants and darkeners are used to suit.

Gray Dyes.—These are graded in 3 fundamental groups like the browns: (1) reddish, (2) bluish, and (3) greenish gray, which by mixture can give numberless shades. These are simpler to produce than browns, for one darkener may be used for all, copperas, which reacts gray with the

ground colors containing tannin, such as alder, willow and bablah. The dyes free from tannin, such as Brazil wood, logwood, fustic, etc., are used for shading. The ground colors can be used singly or in mixture, but always with a vitriol, copperas being the best. The recipes illustrate the influence of the various components on the shading.

RECIPES FOR GRAYS (in liters.)

	Reddish			Bluish			Greenish		
	Light	Med.	Dark	Light	Med.	Dark	Light	Med.	Dark
Willow bark	12	6	4	4	2	..	8	..	..
Alder bark	4	6	8	8	6	8	8	8	8
Brazil wood	½	1	3	..	..	..	..	..	..
Logwood	1/16	⅛	½	..	½	½	1/16	¼	½
Bablah	..	1	4	..	1	4	..	..	4
Elderberry	..	1½	3	1	2	4	..	..	..
Privetberry	..	..	..	..	4	..	..	6	6
Fustic	..	..	..	..	..	..	2	4	3
Indigo-carmine	..	..	..	⅛	..	¼	1/16	½	1

The Origin of Active Lactic Acid in Pine Tan Liquors. W. EITNER. *Gerber*, 1909 [35], No. 833, p. 127.—The author had previously shown (abstr. this JOURNAL, 1908 [III.], 365) that several cases of defective pine tanned leather were due to abnormal swelling in the presence of active lactic acid. In the investigation of a similar case during the last winter, he has again found this acid and traces its origin to a pond of water used only as a reserve winter supply. From the micro-organisms present, forms were separated resembling the B. aërogenes, and pure cultures of these developed active lactic acid fermentation in sterilized extracts from fresh pine bark. In one of the cases previously referred to, the tanner had attributed the mischief to the water. The author's bacteriological examination at that time showed a moderate quantity of organisms (see abstr.). This manufacturer reports no trouble during the last winter, a new water supply being used. It would seem that the water was really to blame in this case. In general, the mineral ingredients of water are of less consequence than the content in bacteria; and examination for these is the more important. The condition of waters in this respect, however, vary greatly with conditions. It is remarkable that in the case in question, the abnormal results are confined to the cold season.

Preserved Eggs. W. EITNER. *Gerber*, 1909, [35], No. 835, p. 156.—The so-called barrelled eggs (Fasseier) have been used in the glacé leather tannage some time. The consumption of egg albumen in dye-printing brought large quantities of egg yolk, as a by-product, into the market. In more recent times, large amounts have been imported from Asiatic countries. There is considerable competition, as well as adulteration, in this article. The poor results sometimes obtained are not, however, so often due to adulteration as to imperfect preservation. Salt is commonly used, 12 to 15%, this is able to preserve fresh egg yolk for some

time in closed vessels, but will not prevent fermentation due to exposure to the air or the presence of eggs already decayed. In using the fermented product, the egg oil separates from the emulsion and makes grease-spots, and the albumen is precipitated and deposits on the leather in lumps, especially on the flesh. Egg yolk is much better preserved by 3% of borax or 1½% boric acid; also ½ to 1% salicylic acid may be used. These, although not expensive, have not been used to any extent by the producers, as they do not contribute to weight. Average analysis of pure egg yolk:

	Hen's eggs	Duck's eggs
Water	54	53%
Fat (egg oil)	28	24
Albumens	18	23

In use, the oil gives the leather flexibility and the albumen finely divides and distributes the oil and itself fills the fiber. From the composition, the hen's egg is best suited for glacé leather and the duck's egg for chrome leather, having more filling power, while the fat liquor makes up the deficiency in oil. The salt preservative lowers the contents of the useful oil and albumen, also water is sometimes added to give the desired consistency. The following analyses of commercial egg yolk show the reduced ratios:

	Hen's eggs		Duck's eggs
Water	61.21	64.43	54.32
Oil	11.27	12.16	18.31
Salt	18.68	14.57	12.51
Albumen	8.84	8.84	14.86

As the oil content is generally used for control, fats are sometimes added to raise the percentage. This works mischief with glacé leather, for the foreign fat aggregates in drops or lumps on making the emulsion and occasions grease spots and uneven dyeing. The addition of soap emulsion is worse yet, this reacting with the alum. For comparison:

1 liter unsalted pure barrelled egg = 66.6 yolks.
1 liter 12% salted barrelled egg = 4.91 yolks.
1 liter 15% salted barrelled egg = 45 yolks.

In practice, 60 egg yolks are reckoned to a liter, which is too high.

Efflorescences on Leather. B. KOHNSTEIN. *Gerber*, 1909 [35], No. 834, p. 141.—These disagreeable consequences of errors in manufacture often do not show themselves until the leather is entirely finished, or even in use. Mineral coatings from alkalies and other crystalline salts may come from an excessive washing of leather with alkali, treatment of the oiled grain with alkalies and salts before grounding with natural dyes, bleaching with lead and tin salts, use of alkaline soaps, and finally from the use of hygroscopic salts (Ba, Mg, Zn) in loading sulphur coatings may appear on chrome leather made by the double-bath process. Light

colored uppers are sometimes blacked at the junction with the soles, by the reaction of the sulphur with the sugar of lead used in bleaching. A separation of free fatty acids upon the surface of leather, giving a disagreeable feel and appearance, is generally due to the decomposition of fats or soaps by free mineral acid. This is most frequent with chrome leather. The use of oils, degras, etc., which have been bleached or sulfonated with acid, may cause this reaction. A similar separation may result from the use of too crystallizable oils. The chrome tanner should use oils stearine free as possible, melting below —10° C., such as neatsfoot oil or sperm oil.

The Employment of Different Types of Evaporating Dishes in Tannin Analysis. U. J. THUAU AND P. DEKORSAK. *Collegium*, 1909, No. 364, p. 228.—The following forms of dishes were tested:— (1) nickel, flat bottom, 84.5 mm. diam., 20 mm. depth, 0.5 mm. thick; (2) glazed porcelain, flat bottom unglazed, size 91.8 x 18 x 2.3 mm.; (3) same, size 71 x 34.5 x 2.5 mm.; (4) glazed porcelain, rounded bottom, size 98.8 x 26 x 1.6 mm.; (5) glazed porcelain, bottom rounded, size 95.8 x 23.6 x 2 mm.; (6) glazed porcelain, spherical, glazed entirely, size 73 x 34.5 x 2 mm.; (7) glazed porcelain, flat bottom, entirely glazed, size 69 x 32.6 x 2.1.

The 7 dishes were each charged with 50 cc. of tannin solution (chestnut ext., 24.5) and the time determined for complete evaporation on the water bath; they were then further heated on the bath and weighed at the end of 3 hours, then heated ½ hour more and weighed again, this last weight proving by further trial to be constant..

No.	Hr.	Min.	Weight dry residue 3 hrs.	3½ hrs.	Per cent. solubles
1	0	42	.2324	.2310	41.7
2	1	44	.2286	.2280	41.2
3	1	45	.2292	.2292	41.4
4	1	09	.2296	.2288	41.3
5	1	09	.2292	.2292	41.4
6	2	01	.2288	.2282	41.2
7	2	15	.2296	.2286	41.3
8	1	55	.2724	.2724	41.0
9		43	.2772	.2744	41.4
10		58	.2748	.2734	41.2

The elements favoring evaporation are metal, large diameter, flat bottom. A previous analysis of the same solution had shown the same result twice as No. 2, which from all comparisons is judged the best form. No. 6 requires more time for evaporation.

A second series of similar experiments was made with dishes, (8) glass, flat bottom, size 72.6 x 28.5 x 2 mm.; (9) aluminum, flat bottom, size 82 x 26.5 x 0.5 mm.; (10) glazed porcelain, flat bottom unglazed, size 90 x 126 x 2.3 mm. The metal dish here also gave the highest residue. The porcelain dish (10) is considered best.

The Use of Nickel Evaporating Dishes for Tannin Analysis. M. SCHELL. *Collegium*, 1909, No. 364, p. 227.—The tests were made upon flat dishes, 85 mm. diameter, 20 mm. deep. It was found that the nickel was appreciably dissolved by the tannin solution according to salinity, from 1 to 2 mgs. being lost in each determination. Further, the metal is thick, cooling slowly, and being somewhat porous, the tare fluctuates with hygroscopic variations. Dishes of hammered silver have none of these disadvantages.

PATENTS.

Artificial Tanned Fabric with Finish Coating and Process of Making Same. U. S. Patent No. 926,525. E. WEINHEIM, New York. A process of forming an homogeneous fabric impervious to moisture, by saturating a fluffy batting of vegetable fibers with bichromate of potassium; then by heat and pressure forcing in a body filling, consisting of a leathery composition of viscous gelatinous matter, oils, fats, metallic salts and alkali. The prepared batting is then dried, and a dense surface coating of patina, of similar composition to the viscous mixture, is applied and becomes incorporated with the surface fibers of the fabric.

Leather-like Surfaced Fabric and Process of Making Same. U. S. Patent No. 926,526. E. WEINHEIM. (Analogous to preceding patent).

Artificial Tanned Fabric and Process of Making Same. U. S. Patent No. 926,527. E. WEINHEIM. (Analogous to previous patent).

Short Cylinder Hide Treating Machine. U. S. Patent No. 926,811. A. H. KEHRHAHN, Frankfort-on-the-Main, Germany.

Process for the Production of a Leather Substitute. U. S. Patent No. 927,198. R. WEEBER, Vienna, Austria. A process for producing a leather substitute, which consists in adding fibrous material to a solution of balata, caoutchouc and gutta-percha, precipitating the agglutinant on to the fibrous material, separating the fibrous material from the solution, adding an oil to make the fibrous material soft and flexible, and forming the material into a sheet.

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ELECTIONS.

The following have been elected members of the Association:

ACTIVE.

N. Grier Parke, IInd., Great Bend, Penna.

ASSOCIATE.

R. O. Nys, 547 Evergreen Av., Chicago, Ill.

ANNUAL MEETING.

The Annual Meeting of the American Leather Chemists Association will be held at Washington, D. C., December 2, 3 and 4, 1909.

COUNCIL PROCEEDINGS.

Abstract of Minutes of Council Meeting Held at New York City, Monday, July 26, 1909.

Mr. Wilson presented a suggestion from Mr. Teas relative to the Council appropriating a portion of the receipts for the support of the JOURNAL. It was the opinion of the Council that the Association could not do better than under the present method, by diverting from the money received from dues the amount necessary to defray the expenses of the JOURNAL.

The Secretary reported the following as to Committee reports:—

Acidity of Liquors: Mr. Alsop submitted his report, which was published in the July JOURNAL.

Color Valuation of Tanning Materials: Mr. Kerr has not yet reported.

Commercial Acids: Mr. Phelan has not yet submitted a report.

Fats and Oils: Dr. Rogers expects to submit a report later.

Leather Analysis: Mr. Veitch expects to submit a brief report before the next meeting of the Association.

Chroming of Hide Powder; Acidity of Hide Powder; Cooling of Extracts for Analysis: Mr. Eachus reported to the Council

that the various reports were expected to be submitted before the annual meeting.

Mr. Small reported as Chairman of the Committee on Filtration that no actual work had yet been done. The Council thought it best to proceed with the work and it was the opinion that an ordinary Quebracho extract, a clarified Quebracho extract, and a Chestnut extract with possibly a Hemlock extract would be sufficient for the determinations.

Mr. Small reported as Chairman of the Committee on the Determination of Ingredients in the Mixtures of Tanning Materials that he had received no definite results from any of the Committee.

Mr. Wilson reported as Chairman of the Committee on Artificial and Natural Acids in Tan Liquors that owing to his change of plans he had been unable and would be unable to have the work done.

The question of holding bi-ennial meetings was brought up and the Council voted that it was the sense of the meeting that bi-ennial sessions are inadvisable.

It was voted that the next annual meeting be held at Washington, D. C., Dec. 2, 3 and 4, of this year.

It was voted that a Committee of Five be appointed to have in hand the program, arrangements of the meeting, consisting of the President, as Chairman, Secretary, and three others to be appointed by them.

Mr. Small brought forward the request of Mr. Seymour-Jones, Chairman of the Committee appointed at the Brussels Convention of the I. A. L. T. C., to make a thorough study of the question of the preservation, cure, disinfection, etc., of hides. Mr. Seymour-Jones has written to Mr. Small requesting our Association to co-operate with the Committee and suggesting that a Committee of our Association be appointed to co-operate and further, to bring the matter to the attention of the packing houses and obtain their co-operation and in addition, to interest the Government in the subject.

It was voted that the Association co-operate with the Committee of the International Association, and further voted that Mr. Small be made Chairman of the local Committee with power to select the members of the Association he wishes to co-operate

in the work and with power on behalf of the Association to negotiate or enter into any arrangements with the packing companies or the Government that he in his wisdom may see fit.

The following twelve names were selected by the Council and on motion accepted as candidates for vacancies in the Council:— Smoot, III, Cushing, Carr, Maxwell, Eachus, Oberfell, Norris, Alsop, Haley, Dean, Griffith, White.

Mr. Norris brought up the subject of requiring chemists to note on their reports the fact of samples not having been taken in accordance with the Association's methods. On motion it was voted that it is the sense of the Council that the Report of the Sampling Committee be altered so as to include a clause providing that the analyst shall in all cases report any violation of the method of sampling in the case of any particular sample which may come to his notice.

It was voted that the President be instructed to write the International Association inviting them to send a representative to the Annual Meeting of the Association.

The Secretary reported the receipt of an acknowledgment from the President and Secretary of the I. A. L. T. C. of bound volumes of the JOURNAL.

On motion the meeting adjourned.

LACTIC ACID IN AMERICA.[1]

By W. H. McLauchlan.

To prepare lactic acid in the laboratory, about 400 grms. of commercial glucose, known to the trade as 70 per cent. grape sugar, are dissolved in about 1200 cc. of hot water, preferably in an agate ware pot. To the hot solution, about 170 grms. of whiting, or any well-powdered calcium carbonate, is added, and 20 grms. of malt, which has been previously boiled a few minutes in 100 cc. of water. The whole is kept simmering gently for half an hour to sterilize the raw materials; it is then allowed to cool to 60° or 70° C., and after stirring well to bring the calcium carbonate into suspension, it is poured into a narrow-mouthed bottle, having a capacity of two or two-and-a-half liters. A little

[1] Read at the Seventh Int. Congr. Appl. Chem., London, 1909.

more water, used to rinse out the calcium carbonate, is poured into the bottle until the volume amounts to some 1800 cc. The bottle is then stoppered with a wad of cotton, and placed in the air bath or incubator, which is kept at a constant temperature of 45° C.

For fermentation experiments, an air bath much larger than usual is needed. This can be easily made from a sheet-iron oven, and the temperature should not vary more than one degree. The metal disc thermo-regulators used for incubators are accurate enough for this purpose, but are not satisfactory with much variation in the gas pressure. After the bottle and its contents have cooled to the air bath temperature it is ready to be inoculated with a lactic acid ferment. The pure culture may be prepared by first sterilizing in a number of test-tubes, sweet milk. These tubes, after sterilizing, are closed with a cotton plug and placed in the air bath. Number one tube is then inoculated with a drop of sour milk; a day later number two tube is started from number one tube, and number three from number two, and so on, until the seventh tube is supposed to contain a pure culture. For experimental purposes one may proceed at once using either sour milk or casein to start the fermentation. Only a few grains are required, and in five or six hours after introducing the ferment, the progress of the fermentation can be noticed by the evolution of carbon dioxide when the bottle is agitated. This shaking should occur every six hours, or oftener, although the bottle may be allowed to stand overnight, and if the fermentation is proceeding properly the evolution of gas upon shaking the calcium carbonate with the supernatant sugar-lactic acid solution will be quite vigorous. Samples of the solution are pipetted out each day and tested for the per cent. of calcium in solution, which indicates the progress of the fermentation and the consequent formation of calcium lactate. At the expiration of a week or ten days the per cent. of calcium remains stationary, or increases very slowly, and a sample is tested to see if any unfermented sugar remains. If this is less than 0.4 per cent., the fermentation may be considered finished. The calcium lactate solution is treated with the calculated quantity of sulphuric acid, and after stirring well, a test tube full is filtered and tested with a drop of sulphuric acid, to be sure that acid sufficient to pre-

cipitate all the calcium, as calcium sulphate, has been added. When this point has been reached the calcium sulphate is removed by filtration. The impure lactic acid in the filtrate can be freed from volatile constituents by evaporating. On concentrating, more calcium sulphate separates out, which must be again removed by filtering. The final filtrate should amount to about one liter of 25 per cent. lactic acid. The acid thus obtained is not perfectly colorless, but can be decolorized with animal charcoal.

If the calcium lactate solution be allowed to cool after the fermentation is finished, calcium lactate, which is much less soluble at ordinary temperatures, separates from the solution. The mother liquor may be squeezed out, and the calcium lactate washed in small quantities of cold water. This washed calcium lactate after being dissolved and decomposed with sulphuric acid yields a colorless strong solution of lactic acid.

The details for preparing lactic acid have been given because the process for making it on a commercial scale is, in principle, identical with the method just given for preparing it in the laboratory. The various operations to be carried out are: 1st. Preparing solution for fermenting. 2nd. Fermenting. 3rd. Decomposing the calcium lactate. 4th. Filtering out the calcium sulphate. 5th. Concentrating.

The Solution.—When the raw material consists of starch-corn (maize), grain, or other material in which the source of sugar is starch, this must first be inverted by the action of dilute acids or malt diastase. In either case the grain must be first ground, and if the inversion is to be accomplished with acid, the grain or starch is placed in a large wooden tank, and sufficient water to agitate the material is added, followed by about 2 per cent. of sulphuric acid. The temperature is raised to, and kept at, 95° C. for five or six hours by means of live steam. When inverting with malt, about 10 per cent. of the weight of the material to be inverted is used. The temperature in this case is 65° C. If glucose or other fermentable sugars are used as raw material inversion is unnecessary. The glucose is dissolved and pumped into the fermenting tank. To the sugar solution is now added enough finely powdered calcium carbonate to neutralize all the acid which can be formed by fermentation from

the sugar, the object being to remove the free acid, as more than 1 per cent. stops the action of the lactic acid bacteria. Calcium carbonate containing free lime may be used, although it is commonly thought that no lactic fermentation would occur with an alkaline substance present. The lactic bacteria require as nutriment a certain amount of nitrogenous matter. This is present in grain, but when fermenting solutions of sugar, this nitrogen must be supplied. Peptone may be used in the laboratory, but gluten meal, casein, malt, or grain are used in manufacturing. This material is generally "digested" in a weak sulphuric acid solution before running into the fermentation tank. The amount used should be such that the nitrogen corresponds to 0.1 per cent. of the sugar. The use of inorganic salts containing nitrogen, nitrates, ammonium salts and phosphates, has been recommended, but seemed unsatisfactory both for a laboratory experiment and in actual practice. When the sugar, calcium carbonate, and nutrient matter have been brought into the tank, water is added, and the solution stirred until the specific gravity corresponds to 15 to 17 per cent. of sugar. In order to sterilize, before starting the fermentation, live steam is blown in through a perforated coil in the bottom of the tank until the temperature rises to 95° C., where it is held for an hour, and then the solution is allowed to cool to 45° C., and is now ready for inoculation with the lactic acid germs. The lactic acid ferment may be prepared as directed for making small amounts of lactic acid, using, however, a large copper can about one hundred liters capacity, kept at the fermenting temperature in a large incubator or box kept at constant temperature by a steam coil. The fermentation tank, made of cypress wood, is ten to sixteen feet in diameter and six to eight feet in height, provided with a steam pipe for heating, which can also be used as the pipe for stirring with compressed air. These pipes are of lead or copper, and there is a lead pipe connection in the floor of the tank leading into a pipe laid along the face of the fermentation tanks, through which the fermented liquor is pumped. The tank is covered, and has a manhole which can also be used to introduce the materials required for making the solution. The tank is also supplied with a thermometer and a spigot from which samples for daily tests are taken. The fermentation should begin in a few hours after

"starting" with the lactic ferment, and should go rapidly the first three days, and then less rapidly as the sugar concentration decreases. Sometimes the fermentation stops before the sugar is used up. In this case the liquor is again sterilized should any foreign organisms be present, and is started again with more of the lactic acid culture. The worst foe to a "clean" fermentation seems to be the butyric fermentation. Should this appear, the calcium lactate is decomposed and hydrogen is liberated, which is responsible for the explosions which occur when a naked light is used in a tank containing liquor fermenting improperly. Some acetic and formic acids are occasionally produced, but in no case should these volatile acids amount to more than 5 per cent. of the lactic acid present. When the fermentation is over, the solution is heated by steam preparatory to pumping to the tank in which the sulphuric acid is added. After neutralization, the calcium sulphate is allowed to settle, and the clear lactic acid drawn to a storage tank. One-half the volume in the tank, containing the calcium sulphate, is still left. To this, weak acid from the filter press is added. The contents of the tank are well stirred, and allowed to settle. Again the clear liquid is drawn off, and the remainder, containing the calcium sulphate and the diluted acid, is sent through a plunger pump to the filter press. The liquor from the press is added to that from the decomposing tank. When the press is full it is washed until the wash water is free from acid, the strong wash waters being stored for washing the calcium sulphate in the decomposing tank, the weak wash water being used in making up new charges. The acid, except that to be used for washing the calcium sulphate, is evaporated to 22 per cent., the strength at which most of it is sold. Occasionally some is sold at 50 per cent. This concentration is accomplished in a copper vacuum pan, supplied with a steam belt or coil and a "juice catcher" between the pan and the condenser. The pan may be heated by exhaust steam. The finished acid is light colored when made from glucose or starch, but dark brown when made from grain or other materials containing coloring matter. The specific gravity of the 22 per cent. acid is about 1.1. The calcium lactate may be crystallized out from the liquor after fermentation, and then washed free from mother liquor and dissolved in a small

amount of water. The washed calcium lactate, decomposed with sulphuric acid, gives an acid light in color, and free from soluble impurities. This operation is not followed in America because the consumer is not particular about the color of the acid, and further, calcium lactate is a difficult salt to handle. It does not crystallize well and is quite soluble even in cold water.

In all chemical processes depending upon a fermentation, it is well understood that a scrupulous cleanliness must be observed; therefore, a lactic acid plant must be arranged so that it can be kept clean and free from all chance of contaminating the fermentation. The floors should be built of cement so that they may be flushed off with water. The fermentation tanks should be placed so that the floors beneath and the walls next them can be easily kept clean. In addition to the inverting, fermenting, and storage tanks, ten or twelve in all, a steam plant, 40-horse-power engine, air compressor, vacuum pan, filter-press, four pumps, a lead-lined acid tank, and iron sulphuric acid storage tank are required. Such a plant could be built for $15,000, and would have an approximate capacity of 100 tons of 22 per cent. lactic acid per month. The demand for lactic acids is not great enough to warrant the establishment of a plant for its sole manufacture. In America, at least, it is made only by concerns engaged in the manufacture of other chemicals as well. Most of the lactic acid is sold to the tanneries where it is used as a so-called "plumper." The hides are heated with dilute lactic acid, which prepares them to receive the further treatment in the process of tanning. Lactic acid has thus a restricted market.

THE CUTCH INDUSTRY OF BORNEO.[1]

Cutch is a hard, brown, brittle substance, and when broken presents a smooth shining surface like anthracite coal. It is used for tanning leather and also for dyeing textiles, black or brown. Sandakan has a prosperous cutch factory, which produced and exported 830 tons in 1907 and 970 tons in 1908. Cutch is manufactured in Dutch Borneo and at Mempaked across the bay from Kudat. The cutch is made by these factories from the bark of the mangrove trees which grow in great abun-

[1] From the Journal of the Royal Society of Arts.

dance in salt marshes, extending inland in various places in North Borneo as far back as one hundred and twenty-five miles. The American Consul at Sandakan says that large fleets of small native boats collect and transport the bark to the factories. The trees after being stripped of the bark, are, as a rule, cut down, split, and chopped for firewood, loaded into small boats, and finally exported to Hong Kong and other ports. The wood makes an excellent fuel for steam launches. The mangrove bark after delivery to the factory is subjected to the treatment found to be most effective in extracting the tannin and reducing it to solid commercial form. Cutch is by no means a new substance, having been used by the ancients for dyeing a permanent black or brown. It is obtained from many species of the acacia. In India they cut the whole tree into chips, which are boiled until the tannin is extracted; then the exhausted chips are taken out, fresh chips put into the kettle, sometimes with leaves and twigs, and the process repeated until the liquor acquires the consistency of coal tar. It is then poured into moulds, where it hardens, after which it is made into balls and wrapped in the leaves ready for market. Cutch of an inferior quality is made from the Areca palm, also from a plant called gambier, which grows in Borneo. It is made and sold by the natives. The value of the gambier exported from Borneo in 1907 was £1,140. Cutch is also largely produced in Sarawak and Dutch Borneo, and goes to increase the exports of these countries. The vast extent of the mangrove swamps in North Borneo, their easy access and the excellent quality of the cutch produced, promises an increasing trade in this useful and necessary product. As the supply of oak and hemlock bark is constantly growing less in the United States, the demand for cutch will increase. The mangrove trees are said to exist in some of the Philippine Islands in abundance, but they have not as yet been utilized.

ABSTRACTS.

The Softening of Dried Sheepskins. L. MEUNIER AND M. HUC. *Collegium*, 1909, Nos. 363-4, pp. 117-9; 221-5.—The sheepskins which are treated at Mazamet by the wool-pullers come in dry form from Australia, South America and New Zealand. On arrival, they are soaked in

water, milled and then de-wooled by the sweating process. In effecting this last, the hides are suspended by the hind-feet from hooks fixed in boards placed at a short distance from the ceiling in closed chambers. The hides then undergo a fermentation which attacks most the horny cuticle and the malpighian layer and consequently permits the easy removal of the wool. The wool is separated upon the beam by the aid of special knives. The de-wooled pelt is then suspended by the hind feet in chambers heated by a current of warm air until it is dry. At this stage it leaves the wool-puller's establishment and is sold to the white leather tanner.

The first operation of the white leather tanner consists in softening with water the dried hide. It is found that the water used in soaking at once becomes milky; it is rapidly enriched with albuminous matters surrendered by the hide to such an extent that after a certain time the liquor acquires a muddy aspect.

Knowing the importance of this loss of substance, we proposed to solve the following problems:

(1) What is the loss of the substance undergone by the dried hide during soaking?

(2) What method is to be employed to reduce this loss?

(3) What improvement in the product manufactured by this method may be realized?

This last point has a special interest, for the Mazamet skins once tanned furnish a leather that is generally lax and this defect is especially marked in chrome leather.

I. *Loss of Substance Suffered by the Skins During Soaking.*—To determine this, we have employed with profit the excellent method recently published by Prof. Stiasny,[1] and which has already been reviewed by one of us (see *Bull. Synd. Gén.*, 1909, p. 57). We judge it useless to reproduce again Stiasny's method of operation; we ought however testify that we are extremely satisfied with its employment. It is in place to earnestly recommend it to the technologists desiring to follow exactly the loses undergone by hide during the different periods of beam-house work.

Our determinations have been made upon the operations of soaking at 6°, 15° and 45°. Some have been effected with agitation, the others without. The hides have been kept in the water (Rhone water, titrating 15°) until they were practically fresh. In each case, the time necessary to attain this result has been noted, the amount of substance lost by the hide has been determined and the results reported for 100 kilograms of dry hide. In the experiments made with agitation, 4 agitations of one quarter-hour each were considered sufficient; the times necessary to freshen the hide were appreciably the same in two trials made at the same temperature, with and without agitation.

The results obtained appear in the following table:

[1] For Stiasny's method, see abstract, this JOURNAL, 1908, (3), 398.

Temperature of water	Duration of soaking Hours	Loss of weight in 100 kilos dry hide Kg.
6° without agitation.....	27	26.41
6° with agitation.....	26	22.81
15° without agitation.....	20	22.81
15° with agitation.....	20	26.41
45° without agitation.....	12	32.70
45° with agitation.....	12	33.46

On examination of these figures, it may be deduced that at ordinary temperatures, the hides lose about the quarter of their substance by the sole operation of soaking in water; by operating with luke-warm water of 45°, the loss extends to a third. Such results need no comment and condemn on the one hand the sweating process for de-wooling, and on the other the desiccation of the de-wooled pelts before passing to the tanner.

It is well evident that the fermentation which has taken place during the sweating, has affected not only the epidermis, but even the dermal fibers themselves, transforming the albuminoid matter of these fibers into acid amides or peptonic products giving with water during soaking, true solutions or rather colloidal solutions. This transformation of the albuminous matter continues during the drying of the pelt in the hot chamber.

It being the case that the sweating process which renders a very fine wool, is the only one employed by the wool-pullers in the region of Mazamet, moreover the drying of the pelts being almost necessary before forwarding to the white leather tanners of Graulhet, we are enforced in respecting local customs to diminish as much as possible this considerable loss of substance.

II. *Research Upon a Method of Soaking Susceptible of Diminishing the Loss of Substance in Dry Skins.*—We have sought to introduce into the water of the soaks a substance diminishing the loss of weight previously specified.

(1) We have at first examined the use of an alkaline substance like sulphide of soda and caustic soda.

(2) We have studied the employment of an acid substance like bisulphite of soda, sulphurous acid, hydrochloric acid.

We shall first give a résumé in tabular form of the results obtained with these different products and shall then discuss these results. The experiments have been made at three different temperatures, profiting by the winter season, with and without agitation. The time necssary for practically softening the hide has been noted. The agitation was made gently during one-quarter hour every 2 hours.

I. EMPLOYMENT OF SULPHIDE OF SODA IN CHARGES OF 2 KG. CRYSTALLIZED SULPHIDE TO A CUBIC METRE OF WATER.

Temperature of soaking bath	Duration of soaking Hours	Loss of weight in 100 Kg. dry hide Kg.
4° without agitation	5	22.29
4° with agitation	5	21.29
16° without agitation	4	17.49
16° with agitation	4	20.53
35° without agitation	2	22.5
35° with agitation	2	21.67

II. EMPLOYMENT OF CAUSTIC SODA IN CHARGES OF 1 KG. TO EACH CUBIC METRE OF WATER.

Temperature of soaking bath	Duration of soaking Hours	Loss of weight in 100 Kg. dry hide Kg.
4° without agitation	4½	24.02
4° with agitation	4½	26.28
16° without agitation	3½	26.23
16° with agitation	3½	24.31
35° without agitation	1½	29.04
35° with agitation	1½	23.57

III. EMPLOYMENT OF BISULPHITE OF SODA WITH A CHARGE OF 4.5 KG. TO 1 CUBIC METRE.

Temperature of soaking bath	Duration of soaking Hours	Loss of weight in 100 Kg. dry hide Kg.
6° without agitation	8	5.32
6° with agitation	8	6.08
16° without agitation	7	9.12
16° with agitation	7	3.79
45° without agitation	4½	12.92
45° with agitation	4½	13.68

IV. EMPLOYMENT OF SULPHUROUS ACID OF DIFFERENT STRENGTHS, THE COMMERCIAL SOLUTION OF SULPHUROUS ACID USED WAS 4.5° BE. CONTAINING ABOUT 10% SO_2. THE FIGURES OF THE COLUMN "CONCENTRATION" REPRESENT THE NUMBERS OF LITRES OF THE ABOVE SOLUTION EMPLOYED IN A CUBIC METRE OF WATER.

Temperature of bath	Concentration	Duration of soaking Hours	Loss of weight in 100 Kg. dry hides Kg.
16° with agitation	1	1½	6.55
16° without agitation	1	1½	5.10
16° with agitation	3	1½	2.18
16° without agitation	3	2	2.18
16° with agitation	5	1½	0.80
16° without agitation	5	1	1.45.

V. EMPLOYMENT OF HYDROCHLORIC ACID OF DIFFERENT STRENGTHS. THE FIGURES IN THE COLUMN "CONCENTRATION" EXPRESS THE NUMBER OF LITRES OF COMMERCIAL HYDROCHLORIC ACID EMPLOYED TO A CUBIC METRE OF WATER.

Temperature of bath	Concentration	Duration of soaking Hours	Loss of weight in 100 Kg. dry hides Kg.
16° with agitation	0.3	1½	3.63
16° without agitation	0.3	2	3.63
16° with agitation	0.3	1½	2.18
16° without agitation	0.5	2	2.18
16° with agitation	1	1	3.01
16° without agitation	1	1½	3.82

From these series of experiments we can draw the following conclusions:

(1) Substances of an alkali nature like sulphide of soda and caustic soda, diminish very considerably the duration of the soaking, but they do not diminish appreciably the weight of substance lost by the hides. The employment of these substances does not completely solve the question.

(2) Substances of an acid nature like bisulphite of soda, sulphurous acid and hydrochloric acid greatly diminish the time of soaking and likewise lower in considerable proportions the loss of weight suffered by the hides. In examining the above figures, it is seen that it is expedient to reject entirely the employment of bisulphite of soda and to retain only that of sulphurous and hydrochloric acids.

(3) If the question is considered from the economical point of view, it is seen that to lower the loss of substance to about 2%, it is necessary to count to a cubic meter of soak liquor 3 liters of commercial sulphurous acid costing 0.3 fr. or 0.5 liters hydrochloric acid costing 0.035 fr.

On trial with a charge of one-half litre hydrochloric acid to a cubic meter of soak liquor it was found that after freshening, the quantity of free acid remaining in the bath corresponded to 0.131 liter of commercial acid

How is the rôle of hydrochloric acid in this phenomenon to be explained? We think it may be conceded that the substances proceeding from the disintegration of the albuminoidal matter of the fibers pass in colloidal solution into the water when the soaking is effected with pure water, but that this solution is not possible in presence of hydrochloric acid and these substances remain in the form of gel in the interior of the hide. The colloidal dissolution in the case of soaking with pure water would evidently be favored by the alkaline products generated during the fermentation.

A last point remains to examine to justify the employment of hydrochloric acid in soaking, that is to investigate if during the liming following the soaking, the substance retained by employing acid does not dissolve anew under the action of lime. With this in view, we have prepared two identical limes; in one was placed the skin refreshened in pure water,

in the other the skin refreshened with an addition of 0.5% hydrochloric acid. The skins were kept 6 days in the limes with occasional agitation. We have finally determined the hide substance dissolved in each lime by Stiasny's method and have found that in each, the proportion was appreciably the same.

1 liter of lime containing 6.48 grms. of substance dissolved from the hide freshened in pure water.

1 liter of lime containing 6.08 gms. of substance dissolved from the hide freshened in the acidulated water.

III. *Modifications Observed in the Manufactured Product When Hydrochloric Acid was Employed for Soaking.*—The hides refreshened by means of water acidulated with hydrochloric acid were tanned with quebracho and sumac, and parallel lots were made with hides refreshened in pure water. We have found that the first lot furnished leathers distinctly superior in body and feel to those from the second lot.

Determination of Water in Tanning Materials. J. JEDLICKA. *Collegium*, 1909, No. 357, pp. 162-4. The author has tested Thörner's new method for water determination in organic products by distillation with higher boiling hydrocarbons, toluol, xylol, petroleum, etc. Very satisfactory results were obtained with oakwood and blood albumin; liquid oak extract gave 2% higher than by the official method, due doubtless to dehydration at a finishing temperature of 180°.

Report of the Analysis Commission of the German Section. J. PAESSLER. *Collegium*, 1909, No. 362, pp. 201-8.—Comparative analyses made in duplicate by 6 analysts are tabulated in detail with the following summary:

	Average Non-tans			Greatest Differences		
	Official Method			Official Method		
Extracts	Amer. White Hide	Freib. Chrom. powder	Zeuthen's method	Amer. White Hide	Freib. Chrom. powder	Zeuthen's method
Chestnut	12.25	12.95	12.9	0.7	0.95	0.7
Pine Bark	11.85	11.75	11.95	0.8	0.1	0.8
Myrabolams	11.2	11.35	11.2	0.45	0.45	0.8
Quebracho, lig., cold sol.	5.75	5.8	5.8	1.15	0.8	0.4
" solid " " .	13.41	13.0	12.7	2.8	1.2	0.7
" " regular..	6.0	6.4	6.15	2.3	1.1	1.4
Average	10.1	10.2	10.1	1.37	0.77	0.8

A brand of Freiberg white hide powder requiring, like the American, chroming before using, was also employed. It had been found that the excessive swelling obtained with earlier brands was due to too fine division and woolly texture of the hide. The new brand was more coarsely divided and of granular texture. This washed readily, but absorbed less tans, showing too coarse a texture.

The individual results were more concordant than any previous, showing that the shake method has been better worked out. Zeuthen's method (abstr. this JOURNAL, 1908 [3], 395) is regarded as a simplification of

the official method. Zeuthen adds 35 gms. water to the hide-powder; to avoid any technical objection to this increased dilution, the chairman (Paessler) pumps the bell dry and reduces the water to 20 gms. The great advantage of Zeuthen's method is that the hide for each determination is washed by itself. No objection can be made to the method since the Commission has already shown that ready chromed hide-powder is equally reliable with white and the method is recommended, using 65 gms. of dry hide for conformity.

A report is also included showing the results of blank experiments in washing hide-powder. In 60 cc. were found milligrams soluble:—

					Freiberg	
	Bosch.	Moll.	Philip.	Sichling.	Sluyter	Knabe
Official method:						
Amer. white powd.	1.1	2.7	0.9	4.2	6.0	7.4
Freib. " "	—	3.9	—	5.9	7.0	7.5
" chrom "	—	3.0	—	4.0	7.0	3.8
Zeuthen's method:						
Freib. chrom. powd.	3.0	4.2	0.0	5.1	6.0	4.1

The results are seen to be variable. At the Freiberg Station Prof. Procter's directions have been carefully followed, without however reaching lower figures. The chairman is of the opinion that these variations do not affect the final analysis, the remaining solubles being precipitated by the tans.

Meeting of the German Section, Frankfurt, June 13, 1909. *Collegium*, 1909, Nos. 363, 367, pp. 119-20, 250-3.—In the discussion of the Analysis Commission's report (above), Dr. Philip reported that in the blank washing tests, he invariably obtained the low figures with all brands of hide powder. In several comparative trials with chestnut and oak extracts, he had found that the Freiberg chromed powder gave higher nontans than the Vienna and American powders. The American article was easier to work with and he requested Dr. Paessler to continue his attempts to make a similar material. Dr. Wegner of Popp & Becker's Institute also found fault with the Freiberg powder in its excessive swelling, going through the cloth on straining and variable results on washing necessitating a blank test for each amount. It was voted that the International Commission be requested to test Zeuthen's method. It was agreed that the Section's Analysis Commission study the determination of insolubles in extracts.

Dr. Paessler reported the observation of frequent corrosion of brass and zinc eyelets in shoes, due to the action of free fatty acids in the leather experiments with oleic acid upon metals showed that Al was not attacked, Fe little, Cu, brass and Sn slightly, Zn very strongly.

He also reported investigation on the loss of fat in leather during storage, amounting to 23% in 2 years in a warm room and not proceeding further; with storage in a cool cellar the decrease was continuous, amounting to 50% in 6 years.

Analysis of Orpiment. M. CAFFIN. *Collegium,* 1909, No. 364, pp. 225-6.—This is an application of Pearce's method for determination of As in minerals. 18 gms. of finely pulverized material, dried at 100° are intimately mixed in a platinum with 12 gms. of a mixture equal parts Na_2CO_3 and KNO_3. This is pressed down and covered with 2 gms. more of the mixture which fill the crucible two-thirds. The covered crucible is heated over a Bunsen flame of 3 cm. and when the reaction is over the product is let cool and finally extracted with boiling water, filtered, and the solution made up to 500 cc. cold. 150 cc. of this are acidulated with HCl, boiled to expel CO_2 and nitrous products, and $BaCl_2$ added to slight excess. The $BaSO_4$ is filtered, dried, ignited and weighed. For the As determinations, 50 cc. of the liquor are diluted to nearly 200 cc., 10-15 cc. HNO_3 added, boiled to expel CO_2, etc., and after cooling made ammoniacal to litmus, then acidulated with a drop of HNO_3 and a few drops of methyl orange added. The liquor is then exactly neutralized with $N.Na_2CO_3$, then an excess of 1.8 cc. Finally, drop by drop, a neutral solution of $AgNO_3$ is added till precipitation ceases. After settling ½ hour in the dark, the precipitate is filtered, washed with cold water and dissolved in $0.1N.HNO_3$ (Cl-free). Several drops of ferric sulphate are added and the solution titrated with 0.1N. sulphocyanide. 1 cc. of this = 1 cc. $0.1N.AgNO_3$ = 0.0025 gms. As. During the precipitation and filtration, the silver arsenate should be protected from daylight. Check analyses:

Sulphur	39.02	49.2	39.41
As (above method)	60.97	49.9	60.16
As (mg. method)	61.04	49.8	60.24

A Tan-Stuff Reaction. M. PHILIP. *Collegium,* 1909, No. 367, pp. 249-52.—for the qualitative examination of tannins, one generally uses Procter's tables or Stiasny's formaldehyde reaction. Besides these a reaction now little used, first described by Eitner and Meerkatz in *Der Gerber* for 1885, can give good service. The extract to be examined is dissolved in water to a tan content of about 2% and 100 cc. of this solution are boiled several minutes after addition of 0.5 gms. conc. H_2SO_4. After cooling, 20 gms. NaCl are added, and the whole filtered. To 15 cc. of distilled water and 10 drops yellow ammon. sulphide in a test-tube, 1.5 to 2 cc. of the extract filtrate are added and shaken. The precipitate with chestnut extract is at the beginning brown, then reddish with a blue shimmer; with oak extract it is yellowish brown; the supernatant liquids are respectively bordeaux red and orange. The reaction requires very careful work for its original application to distinguish chestnut and oakwood extracts and is not always reliable, but may be used for other tans. The following tanning materials also give precipitates: Oak bar, first yellow, later brown; valonea, yellowish green, later chamois; knoppern, yellowish, later red-brown; myrabolams, greenish-yellow; dividivi, bright greenish-yellow; hemlock, yellowish-brown (slow); malet, yellow-brown; mimosa, reddish-white. No precipitate results with que-

bracho, mangrove, pine (at times slight turbidity), catechu and gambier. This reaction can be used to detect myrabolams, dividivi, malet, etc., in quebracho extracts. As in the formaldehyde reaction, only the pyrogallol tans react, while the catechol tans in general give no reaction. The test is applicable to sulphited or otherwise treated extracts.

Investigations on Iron-Gallate Inks (Tenth Communication); **Determination of Tannic and Gallic Acids.** F. W. HINRICHSEN AND E. KEDESDY. *Mitteilungen aus dem Königlichen Materialsprüfungsamte zu Gross-Lichterfelde-West,* 1909, Heft 1, through *Collegium,* 1909, Nos. 365-6, pp. 233-7; 242-8.—The authors have earlier shown that the content of gallic and tannic acids in an ink may be determined by acidifying the liquor with HCl, extracting with ethylacetate and weighing the evaporated extract. The present official requirements for an ink of Class 1 specify "at least 30 gms. to a liter of gallic and tannic acids which are derived wholly from gall-nuts." The authors have tested their analytical method on gall-nut extract. After acidifying with HCl, the solution was extracted with ethyl acetate, this extract evaporated in a vacuum and dried at 105-110°. Two samples of 25 cc. each yielded thus 0.7027, 0.7479 gms. The residue dissolved in water to a clear brown solution. The residual gall-nut solution after exhaustion with ethyl acetate and neutralization with Na_2CO_3, still gave a dark color with $FeCl_3$. Pure tannic and gallic acids do not do this. The authors have previously shown that tannic acid may be determined by its iodine absorption, the ratio being constant for amounts below 0.4 gm. This method was used to determine the tannic acid in the acetate extract from gall-nuts, parallel blank tests being made with pure tannic acid. 30 cc. of an iodine solution containing 30 gms. to the liter were added to the assay together with 2 gms. $HNaCO_3$ and the whole let stand in a closed flask 24 hours, then titrated back with thiosulphate.

	Cc.	Gms.	Cc. Iodine Excess	Cc. Iodine Used
1. Tannic acid	10	0.0938	14.5	15.5
2. " "	15	0.1407	7.6	22.4
3. " "	15	0.1407	7.8	22.2
4. Gall-nut ext. I.....	10	0.0703	17.9	12.1
5. " " "	20	0.1406	7.0	23.0
6. " " II.....	10	0.0748	17.4	12.6
7. " " "	20	0.1496	6.5	23.5

The proportional computation for the tannic acid in the extracts I, II, on the basis of titrations 1-3 give 0.716 and 0.743 gms. as compared with 0.7027, 0.7479 gms., the weights of the dried extracts. It is concluded therefore that the ethyl acetate extract from gall-nut solution consists essentially of tannic and gallic acids, and that the method is reliable for this material.

Myrabolams and dividivi are next in importance in iron ink manufacture. Experiments similar to the above were made with aqueous extracts of

these materials. With myrabolams, the fresh aqueous extract gave up 72 to 74% of its solubles to ethyl acetate. The aqueous solution on standing however, showed itself very unstable, continuously separating sediment for weeks. Moreover the acetic ether extract varied considerably in amount when made on the same day. It was remarkable that this extract when dried did not wholly re-dissolve in water, 15 to 30% remaining insoluble. On titrating the solution with iodine, about 60% of the solubles computed as tannic acid.

It has been shown in earlier researches by the authors, that tannic acid may approximately be determined by titration with $CuSO_4$. The aqueous solution of the acetate extract from myrabolams was treated with a measured excess of $CuSO_4$ in presence of $CaCO_3$, and then titrated back with standard tannic acid, the end-point being ascertained by spotting with $K_4Fe(CN)_6$. According to this titration, the extract contained from 80 to 100% tannic acid.

A third method of estimation of tannic acid is colorimetric, using ammon. molybdate. The above extract gave 62.5-68% by this method.

An aqueous extract of dividivi yielded 37.5% of its solubles to ethyl acetate, which last extract analyzed 70-80% of tannic acid by the iodine method. Pine, oak and mimosa extracts yielded 12.9, 8.8 and 15.5% of their solubles to the acetate and the dried residues were nearly insoluble in water.

From the above results, it would not be possible to distinguish the source of the tannic acid in an ink, hence the specification for official examination requiring gall-nut tannin is futile and should be dropped.

The Constitution of Tannins. M. NIERENSTEIN. *Ber. Deutsch. Chem. Ges.*, 1909 [42], 1122.—The results of further researches on penta-acetyl-leucotannin (abstr. this JOURNAL, 1908 [3] 149,) are described. (1) On saponification with dilute H_2SO_4, gallic aldehyde and gallic acid result. (2) On oxidation in acetic acid solution with potass. persulphate and dilute H_2SO_4, a dark red powder is formed which is named purpurotannin; it gives naphthalene on distillation with Zn dust, but analyzes higher in carbon than purpurogallin or purpurogallin carbonic acid which contain the naphthalene nucleus. (3) On oxidation with $KMnO_4$ in dilute H_2SO_4 solution, trioxyglutaric acid is obtained, indicating a carbon chain containing 3 hydroxyl groups which accords with the author's formula.

The Manufacture of Brown and Black Waxed Leather by the Latest Improved French Process. *Ledertechn. Rundschau*, 1909, Nos. 18-23, pp. 137-9, 147-8, 153-5, 163-5, 169-71, 179-81.—Green or salted hides are best, working better and giving fuller leather in the sides. Soaking is carried out in well-cleaned pits in spring water which is preferable to river water, being without sediment and cooler, especially in summer. Dried hides are soaked 3 days with daily turning in the same water. Green hides receive 2 fresh waters and go to the lime on the second day. Strong salted

hides have fresh water daily, light salted twice the first day, all receiving 3 waters.

Liming.—Three limes are used, the normal process being 4 days to each for green hides, 5 for salt and 6 for dry. In North America, and especially in France it is thought best to lime as little as possible to save hide. The three-lime system is also used, the last always being freshly charged and after once using becoming the second lime, and so on. When all 3 limes are freshly prepared, 100, 160 and 250 liters of slaked lime are used to 10 hectoliters of water for the first, second and third limes respectively. In the first 2 limes the hides remain 2 days each with daily turning and 1 hour draining; in the last lime the hides stay with daily turning until they just yield the hair, 4 days or less. They are then dehaired from warm water. Here there can certainly be no loss of hide, but it is questionable if there is sufficient raising; after only 8 days of liming, it must require skillful workmen to remove the hair without injury to the skins. Such leather must be tough, durable, and of good appearance but cannot take up as much tannin or fat as longer limed hides.

After dehairing, the hides are left in water of 25° R. for 15 minutes, then rinsed and piled flesh upward, lying 12 hours and are then shaved, They are left in water of 12-15° R. 6 hours or over night, worked again mechanically on the flesh, watered again, smoothed with an iron, weighed, watered 4 hours, and finally worked on the grain. After 4 hours soaking, followed by draining, they are ready for tanning and require no bating, being free from lime.

Tannage.—Hides treated as described are not open in texture and must be cautiously tanned at first and very gradually, else the surface is prematurely tanned and the interior cannot be reached. If upper leather is to be made requiring a flexible grain, the acid formation must be prevented in the first 3 vats by use of suitable tanning materials. A system of 4 handler vats may be used followed by a *"versteck"* vat, one *"versenk"* and one layaway; or 6 handler vats with one *"versenk,"* and one layaway; or 8 handler vats followed only by a lay-away. In the 4 vats system, the fourth or best vat is freshly prepared for each lot and becomes the third after being once used and so on down to the first vat which after use is emptied. The liquor for the fourth vat is taken from the so-called "sourpit" (a misnomer). This has a false bottom covered with sacking, over which is placed a 50 cm. layer of fresh bark and above this spent bark from the *"verstecks"* and lay-aways. The bark is leached 8 days before drawing off the first extraction. The pit is then filled with the third leaching from another pit and after 8 days this second leaching is drawn off and replaced by fresh water for the third leach.

The first handler vat, after removing the bark present, is diluted with the third leaching to 1° Bark. The butts are entered and agitated for 2 hours when the flesh begins to darken, which is the sign for shifting to

the second vat. This, the previous third vat, has been freed from bark and diluted with the third leaching to 1¼—1½°. The hides are agitated 1 hour when the flesh lightens and 10 kg. fine ground oak bark are added and after ½ hour another equal portion during agitation which is kept up ½ hour more. The hides are then taken out, piled, let lie one-half hour while 10 kg. more bark is stirred into the vat. The butts are then laid in flesh up and left lie 2 hours. They are again taken out, piled with the grains together, while 20 kg. half-fine oak bark are stirred in during one-half hour when the hides are replaced. A fine regular grain now begins to show. At the end of 6 hours, 20 kg. medium fine oak bark, the hides replaced and left rest over night. The second day 20 kg. chopped oak bark are added in the morning and 20 kg. coarse ground bark in the evening, the third day 20 kg. same morning and evening; the fourth day, 20 + 30 kg., the hides then remaining in rest through the eighth day. For the entire 8 days 200 kg. oak bark have been used for 100 skins of 500-600 kg. green weight. The progressive addition of the bark with increasing coarseness, permits a gradual and uniform tannage. The frequent turning and piling are much more efficient than continuous agitation, which is apt to dissolve hide in weak liquors. For this apparently troublesome method 2 men suffice for a production of 300 hides a week with the assistance of another during the first stage. The third vat is cleared of bark, adujsted to 2½-3°; so many foreign substances however affect the gravity, a test by taste is best, comparing with the second vat. 20 kg. coarse oak bark are added, 2/3 the hides entered, then 10 kg. more bark and the rest of the hides. The hides are pressed down, and 10 kg. more bark put on top. The same additions are made daily for 4 days, the hides being turned, drained an hour and laid in again without agitation. They then remain without turning 6 days more (4 in summer). Each morning, however, they are examined and the bath weakened or strengthened should the hides be unduly swollen or fallen. The fourth vat carefully cleaned is half filled with the first leaching and brought to 3.5 to 5°. The hides after rinsing from the third vat and draining 2 hours are entered with 40 kg. coarse bark; this addition is made daily for 4 days, when the hides lie 4 days more finishing the fore-tannage, 27 or 29 days total.

"Versteck" Vat.—This is used to avoid too sudden a transfer to the pits. This vat is filled 20 cm. deep with the second leaching, and the hides are laid in grain up, each hide being dusted with 4 handfuls of fine bark; more liquor is added, if needed, that the hides may half swim. Such a vat, receiving the hides from 2 fourth handler vats requires 500 kg. bark for 200 hides. These remain here 14 days, the upper hide, flesh-up, being covered with 15 cm. of lately spent bark.

"Versenk" Pit.—This is preliminary to the real pit tannage. The pit is larger than the handler vats and takes the quantity of 2 *"versteck"* vats. The bottom is covered with a 5 cm. layer of fine oak bark. The hides are laid in singly, grain up and dusted with fine bark. The upper

hide, flesh up, is covered 5 cm. deep with bark. There should be 30 cm. space left at the top, and this is half filled with recently spent bark. The pit is carefully filled with the first leaching. For 400 hides, 500 kg. oak bark are used. The grain is still tender and no load beyond the layer of spent bark should be used. Here the grain becomes tanned through, a point to which our tanners give little attention. If not well tanned, it in time becomes dark and brittle. The hides remain 4 weeks in the *"versenk"* but no more; they are rinsed in weak liquors and hung to drain for 24 hours grain to grain. The spent bark from the *"versteck"* and *"versenk"* are extracted in the third leach.

Layaway Pits.—These are round, 2.5 m. wide and deep for 400 medium hides. The bottom is layered 15 cm. deep with recent spent bark, then a layer of lay-away bark. Fine ground oak bark is used for dusting, which is first moistened with the first leach liquor to prevent the settling of fine dust. Coarse bark is not suited for the layers for it presses into the grain, especially when trodden. The hides are laid in folded lengthwise, grain inside, which must all be in contact with bark. Care must be taken not to fill up vacant spaces with bark as is done by unskillful layers. Above is a 5 cm. layer of fresh bark, then 25-30 cm. lately spent bark. The top is covered with boards, weighted with stones and steeped with liquor from the first leach. The layaway stands 2 weeks, and is then drawn. Ordinary hides of 5-6 kg. are then tanned, medium hides of 7 kg. are laid away again for 50 to 60 days, and 8 kg. hides a third time for 2 to 2½ months. The dusting is lighted in the second and third lay-aways. The entire length of tannage for the three weights of hides is then, 4½, 6 and 8 to 8½ months, a long time for calf, but hide has been saved by the light liming and no bating. For each hide, 7½ to 8½ kg. bark are used for dusting in the lay-aways.

Currying.—Fleshing before tannage in order to save tan and hasten the process is only proper in rapid tannage with concentrated liquors. In the slow, uniform tannage described above, the protection by the flesh is beneficial. After tanning, the fleshing is done with the knife on the beam and not when whitening on the table. Strokes are best taken crosswise, requiring skill. The leather is then soaked 24 hours in cold water containing a little tan liquor, then drummed 25 min. in warm water, and are next stretched or set on the table, which is covered with degras when the grain side is worked. The grain is next smeared with an emulsion of 1 part soap, 4 parts water, 8 parts whale oil and left lie 2 to 3 days, which is essential. For the flesh, 30 parts degras, 7 grains soap, 10 soft tallow and 7 water are used. The leather is then dried and let lie 8 days to 4 weeks. The excess of fat and soap paste is then scraped off and the leather moistened with soap water for whitening; after whitening, the grain is lightly worked. For brown waxed leather the flesh is simply glazed or if preferred, first treated with an emulsion of 1 kg. Marseille soap in 10 liters water together with ½ kg. tallow, 1/5 kg. wax, ½ kg. whale or olive oil. For black waxing, 5 parts lamp black are soaked with

10 parts boiled linseed oil, and then rubbed up on the stone with 20 parts more oil, then is stirred in a melted mixture of 3 parts mineral wax, 30 parts seal oil and 20 parts soft tallow; 1 part ox-gall can be added if desired. The leather is laid on the table flesh up and the wax applied with a brush. After lying piled 8 to 12 days, the leather is dried and glazed; the first coat with a brush, the second with a sponge. The first glaze is made from 1 kg. gelatine mass, ¾ kg. neutral soft potash soap, 1/8 kg. (1/5 in winter) linseed oil, 20 gms. aniline black with 50 gms. acetic acid dissolved in ½ liter water. The second glaze contains 1 kg. gelatine mass, 1 liter water, 20 gms. black soft soap, 100 gms. soft tallow, 100-200 kg. boiled linseed oil. The gelatine mass is made by boiling one part glove leather offal in 10 parts water 3 hours, filtering, and letting cool to a jelly.

PATENTS.

Leather-Staking Machine Table. U. S. Patent No. 927,609. F. F. SLOCOMB, Wilmington, Del.

Process of Making Patent-Leather or Artificial Patent-Leather. U. S. Patent No. 928,235. G. R. DEMONTLORD, Boston, Mass. A process of making patent-leather or imitation patent-leather, which consists in preparing a solution of nitro-cellulose, a solvent, a vegetable oil, alcohol, glycerine, spirits of turpentine, and a suitable pigment or dyestuff, immersing the leather or fabric into ethyl acetate, coating the surface of a glass-plate with one or more layers of the same solution, uniting the leather or fabric with the coatings on the glass-plate by pressure, then drying the leather or fabric while on the glass-plate, and finally removing the coated leather or fabric from the glass plate.

Marking or Printing Means for Leather-Skiving Machines. U. S. Patent No. 928,514. R. P. GRANT, Boston, Mass.

Attachment for Skiving-Machines. U. S. Patent No. 928,755. G. A. HENDERSON, Marblehead, Mass. Attachment for sharpening the knife of the machine.

Leather Dressing Process. U. S. Patent No. 929,552. G. W. CHILDS, New York. A process for treating leather after it has been tanned, which consists in impregnating the leather with a liquid dressing of from 1.05 to 1.3 specific gravity, heated above atmospheric temperature, and containing inert solid matter residue of waste tanning liquor mixed with active tanning liquor, and, while the leather is still moist from the tanning process.

Work-Support for Leather Working Machines. U. S. Patent No. 929,772. T. H. MARRINAN, Woburn, Mass.

Method of Obtaining Decolorized Tanning Extracts. French Patent No. 395,499. E. W. TILLBERG. Milk is added to the extract, and on heat-

ing the mixture, the coagulation of the albumen carries down the insoluble matter of the extract.

Method of Tanning Sole Leather. French Patent No. 396,025. Soc. Anon. des Mat. Tannantes et Colorantes. The hide from the beam-house is first treated in a weak solution of formaldehyde, and then tanned in a wheel with extract. It is then dried, and given another tanning in the wheel.

Production of Artificial Leather. English Patent No. 4130. H. W. Lake, London, England. Trimmings from untanned hides are shredded and tanned in the shredding machine by a tanning agent. This product is pressed into sheets and dried.

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Volumes I, II, and III of the JOURNAL, bound in half leather are now ready for distribution. Price $6 per volume delivered.

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CHANGE IN ADDRESS.

Dr. J. Gordon Parker.
New address—176 Tower Bridge Road, London, S. E., England.

ANNUAL MEETING.

The Annual Meeting of the American Leather Chemists Association will be held at Washington, D. C., December 2, 3 and 4, 1909.

DEKKER'S MONOGRAPH OF THE TANNINS.[1]

By W. W. Stockberger.

The completion of Dr. Dekker's monograph of the tannins makes available a reference work of much value from both technical and purely scientific points of view, although the fact that it is written in the Dutch language will materially reduce its usefulness to a wide circle of readers.

Part I., which appeared in 1906, is devoted to (1) Bibliography, (2) Distribution of tannin among plants, and (3) Physiology.

The bibliography, though not complete, contains approximately two thousand titles and is brought down to 1906. The arrangement of the plant names follows that of the Engler Syllabus. Brief notes giving the sources of the plant, per cent. of tannin when known and references to the bibliography accompany the larger number of species mentioned. Some interesting general conclusions are drawn relative to the distribution of tannin among plants: The *Gymnospermae* are extraordinarily rich in plants with high tannin content; in the *Monocotyledoneae* tannin seldom occurs except in the *Palmae*; in the *Dicotyledoneae* the tannin producing families are very numerous, *e.g.*, very rich in tannin are the *Salicales, Fagales, Polygonales, Rosales, Geraniales, Sapindales, Myrtiflorae, Ericales* and *Ebenales.*

Under "physiology" the author devotes a chapter to the methods of research, gives a resumé of the literature of the distribution of tannin in the plant and in the concluding chapter discusses the part played by tannin in the plant economy.

Part II., published in 1908, is concerned with (1) Chemistry

[1] Dekker, J., De Looistoffen, botanisch-chemische monographie der tanniden. Bulletin van het Koloniaal Museum te Haarlem, No. 35, 1906, pp. vi + 220; No. 39, 1908, pp. 241. Amsterdam, press of J. H. de Bussy. Price of each part 1.50 f.

of Tannin, (2) Quantitative Analysis, and (3) Use in the Tannery and Dyehouse, in Medicine, etc.

The first chapter of Part II. presents an historical review of the literature dealing with the chemistry of the tannins and tannoids. This is followed by a chapter of eighty-five pages on "the chemical nature of the tannins," in which are presented the methods of preparation, principal reactions and the chemical composition of the tannins in the chief tannin-producing plant families. In a tabular summary, the various tannins discussed are grouped according to their relationships in a form convenient for reference.

Under "quantitative analysis" seventy-eight methods of estimation are summarized. The work is concluded by a brief chapter on the technical uses of tannin.

ON THE ESTIMATION OF GLUCOSE IN LEATHER.[1]

By H. G. Bennett.

The determination of glucose in leather is undoubtedly one of the most tedious operations of the leather trades chemist, involving as it does the extraction of the leather with petroleum ether, then with water, and finally the detannization of the aqueous extract. It is evident therefore that there is a need for an accurate and quick method for the actual estimation of glucose in the detannization solution. The I. A. L. T. C. were doubtless wise in deciding that the gravimetric method, being the most accurate, should be the "official" method of the Association, but the writer would venture to suggest that the use of the method of Wood and Berry, (Proceedings of the Cambridge Philosophical Society, Vol. XII, Part II,) should at least be a permissible alternative, as it presents some advantages in rapidity over the gravimetric method.

For the convenience of those who have not come across or used this method, the following short description will perhaps be useful:—

The detannized solution is heated with the Fehling's solution in precisely the same way as in the official gravimetric method,

[1] From *Collegium*.

and the cuprous oxide is then filtered off on asbestos felt in a Gooch crucible and washed with boiling water. It is then transferred to a wide-mouthed stoppered bottle already filled with carbon dioxide. The last traces are washed through the Gooch with 25 cc. of 2½ per cent. ferric sulphate solution in 25 per cent. sulphuric acid, and the stopper put in the bottle. A few seconds shaking at once causes the cuprous oxide to dissolve, reducing an equivalent amount of ferric sulphate to ferrous. This is then titrated with a standard solution of potassium permanganate of such strength that 1 cc. oxidizes the ferrous salt formed by the reducing action of an amount of cuprous oxide containing 0.01 gm. metallic copper. The actual strength is just over 5 gms. of potassium permanganate per liter; it is standardized by weighing the copper obtained by reducing the cuprous oxide from 10 cc. of a ½ per cent. glucose solution, and titrating duplicates.

The following results show figures obtained by two independent workers who each used the gravimetric, simple volumetric, and Wood and Berry method on the same sample of leather.

	Method		
	Gravimetric	Wood and Berry	Volumetric
Observer (1).....	15.7	15.3	16.7
Observer (2).....	15.7	15.3	16.3

It will be seen that the new method gives quite concordant results which are, however, slightly lower than those obtained by the official method.

THE INFLUENCE OF EXTRACTS ON TANNING METHODS.

By Simon C. Hemie.

The past twelve years have witnessed a decided change in the list of tanning materials available for vegetable tanning, and this change has occasioned a change in conditions which has been more radical than any change made during the long previous history of the tanning art. Twenty years ago, the introduction of heat in the leach house caused changes in tan liquors which were generally anticipated by the same progressive minds that favored hot leaching. Many of their imitators however simply followed

the example of hot leaching without giving thought to this influence on their liquors, until the influence was reflected in the character of the product; they then sought the trouble and more or less quickly adjusted their methods to meet the changes in the composition of the liquors.

The use of extracts of all kinds in this country during the past twelve years has developed to a wonderful degree. In addition to extracts, the use of imported tanning agents such as mangrove bark, myrabolams, valonia, etc., has had almost a parallel growth during the same period. The influence of these new agents upon the finished leather is of course obvious, but in many instances the possible influences in all directions, upon the method of manufacture were not anticipated to the extent of anticipating changes in methods until such changes became imperative. The influence of color, and of the distinctive leather making characteristics of each material, were too often the only influences expected; frequently the matter of combinations was made the subject of experiments, and some information was derived from these.

The change in the ratio of tannins to the non-tanning materials in the liquors of tanneries in which extracts were being introduced, was quite generally overlooked, and to this day is not recognized in many tanneries as being a factor responsible for various troubles. For years, one might say for centuries, the tanner has been used to the liquors derived from our native mild tanning barks. His axioms, rules and precedents have been evolved from them, and his experience with them has resulted in an almost automatic intuitive disposition to properly change causes when recognized effects became apparent. The introduction of hot leaching caused a change in the nature of his yard liquors; but this change was toward a condition in which many yards with cold leaching were often found. The hot leaching pulled out the non-tanning matters from the bark and served to decrease the ratio of tannins to non-tannins in the liquor; many cold leaching yards encountering an extra heavy tannin sappage by the hides, would often become in a similar condition, so that hot leaching tended toward a state of conditions in the liquors,

which had been previously encountered, and which the tanner knew how to overcome.

The introduction of extracts and liquors made from materials rich in tannin, caused a change in liquor conditions different from any in the experience of the bark tanners; the extent of the change being of course dependent upon the percentage of the new tanning materials used in the liquor. With the use of a large proportion of extracts or rich tannin bearers, it is possible to get a liquor in which the proportion of tannin to non-tannins is relatively greater than is possible with a liquor made from our native hemlock or oak barks. Tanning with these liquors so rich in tannin could not be conducted by the same methods in use with straight bark liquors, and this was slowly recognized.

The tanner who continued with the extract liquors his previous practices as to barkometer strength of liquors, time on the layers, and amount of liquor run to the sewer, found sooner or later that his leather was not the same as his previous product tanned with liquors derived from barks. While he endeavored to give his liquors the amount of tannin previously derived from bark, yet in supplying this tannin by means of extract he was not supplying the so-called non-tanning matters which accompany the tannin leached from the native bark.

The changed liquor conditions were manifest in many ways; the leather was not so plump, it tanned quickly and in many instances was hard. The purity and lack of sediment in many of the extracts, aided the natural characteristic of the specific tannin to penetrate rapidly, and this quick penetration served to quickly tan the hide before the desired plumping could be effected by the natural plumping acids present in the liquors. With the continued use of the extracts and the persistent adherence to bark liquor methods, these natural acids began to decrease, and under these conditions a slower tanning liquor was more desirable than ever.

The insolubles of our native barks serve at least one purpose in protecting the leather in the layers from a too hasty action of the liquor. This virtue may easily become a fault however if there is an excess of insoluble matter deposited on the leather.

To overcome this fault in some extracts, clarification is resorted to; and when certain inorganic compounds are used there is the possibility of their influence on the leather. Certain very soluble inorganic salts have a softening action on leather, and also tend to retard plumpness.

Following the previous program as to the amount of liquor sent to the sewer, will, in a yard made up largely from extracts, result in a constantly increasing ratio of tannin to non-tannins. This was recognized by the pioneers in the use of extracts and the amount of liquor run to the sewer was changed to meet the new conditions.

Extracts have come to stay as long as vegetable tanning is with us, and tanning methods must be adjusted to these new agents. The quality of the leather need not change because of extracts; extracts have been used to make leather of just as high quality as any ever made by straight native barks. Aside from color and clarification qualifications adverse criticism of extracts as tanning agents should be obsolete, and the methods of using the extracts should receive the critical and studious attention of the opponents of extract tanning.

Almost any yard condition favorable to a good product with bark liquors can be duplicated with extracts. Non-tanning matters may be increased by limiting the amount of liquor sent to the sewer, or by the combination with extracts or low grade tanning materials containing a high percentage of non-tanning matters. The duplication of a bark yard known to produce good leather, will generally result in the disappearance of those troublesome tendencies in the course of tanning which are generally considered as characteristic of extract tannage; although the water supply and the method of clarification of the extract may introduce complications requiring special treatment for each tannery.

ABSTRACTS.

The Tannin of Maletto'Bark. (Eucalyptus occidentalis). J. DEKKER. *Archives Néerlandaises des Sciences Exactes et Naturelles.* Serie II, Tome XIV, 1909, p. 50, reprint *Collegium*, 1909, Nos. 370-3.—This material

was chosen for study as its use in Europe has greatly increased since 1904 and moreover little is known concerning those tannins including those of the *Eucalyptae,* which impart a red color. The author gives a full botanical description extracted from F. von Mueller's *"Eucalyptographia; a descriptive atlas of the Eucalypts of Australia and the adjoining islands; Melbourne, 1879-1884."* The bark of this tree (which is 80 to 100 ft. high) is exported to Europe from Australia as "Mallet." Van der Weerd (*Pharm. Weeksblad v. Nederland,* 1906, 322) has given a detailed macro- and microscopic description of the bark which is quoted at length.

The powdered mallet used in these researches analyzed 31.7% tannin, 35.7 insoluble, 13.4 water, 5.74 ash, 0.44 albumins, 19.17 carbohydrates, 8.1 pentosans. The isolation of a tannin in the pure form is not a simple matter. Trimble's method of extracting with ethyl acetate did not prove practical with mallet nor was acetone more satisfactory. The best solvent for mallet tannin was found in 96% alcohol. On evaporation of the alcoholic extract, a brown product is obtained which is readily pulverized and is only slightly soluble in ether, ethyl acetate and acetone, especially this last, even on boiling. In water, the dried extract is almost totally soluble. The method of purification of tannins by precipitation with acetates of lead was rejected as liable to give impure products. The author believes the erroneous view of considering tannins as glucosides was due to defective preparations by this method. Löwe's method of salting out the aqueous solution was tried but the product persistently retained salt and contained reducing sugars. The best method was found in fractional precipitation of the alcoholic solution by ether. The dried extract was dissolved in twice its weight of absolute alcohol and precipitated with half volume of ether giving 32% (of original extract) precipitate (I). To the filtrate was added three-fourth volume ether yielding 22% precipitate (II). (I) was found to contain 12% reducing sugars (calculated as glucose) while (II) was free from sugar and was taken to represent the pure tannin.

Mallet tannin is a cinnamon-brown powder, decomposing without fusion on heating, readily soluble in water, ethyl or methyl alcohol. The solution behaves as colloidal, giving a syrup on evaporation. In contrast to most tannins, this is little soluble in ethyl acetate or acetone. Reactions (1% Solution):—$FeCl_3$, a dull green solution which reacts for ferrous salt; $AgNO_3$, ppt. giving metallic Ag on heating; Fehling's sol., reduced on heating; $K_2Cr_2O_7$, after a time. brown ppt.; quinine sulphate (5%), grey ppt.; Gardiner's reagent ($[NH_4]_2MoO_4$, 5%, NH_4Cl, 25%) brown ppt.; Runge's reagent (alkaline sol. PbO), deep brown color; NH_3Ag, and NaOH red color, darkening in the air; mineral acids and concentr. saline solutions, ppt. unchanged tannin.

Four combustions gave

	Calc. for $C_{19}H_{20}O_9$
C = 58.21	58.16
H = 5.38	5.10

Acetylization gave a product which by combustion and acetyl determination (Sisley) computed as $C_{38}H_{28}O_{17}(C_2H_3O)_{10}$, a dehydration also having taken place. By treatment of the tannin with benzoyl chloride followed by alkali, a derivative was obtained analyzing $C_{19}H_{15}O_{12}$-$(C_6H_5CO)_5$ which is explained as resulting from an oxidation. An aqueous solution of the tannin gives a flocculent precipitate with excess of Br water, which appeared to contain fixed Br not removable by boiling lime water. No satisfactory analysis could be obtained of the compound which on standing gave off free Br. On boiling the tannin with dilute HCl a small amount of gallic acid was formed, but the principal product is "mallet red," nearly equal in amount to the tannin used. No CO_2 was evolved nor could sugars be found. Mallet red is a vermilion-red, amorphous, insoluble powder which is assumed from its analysis to result from the dehydration

$$3C_{19}H_{20}O_9=C_{37}H_{30}O_{22}+5H_2O.$$

There is nothing in the bibliography concerning hydroxyl groups in tannin reds; the authors obtained by acetylizing the mallet red a product analyzing $C_{87}H_{35}O_{22}(C_2H_3O)_{15}$, showing that the 5 hydroxyl groups of the original tannin have been retained in condensation. It is probable that oxygen of ketone groups take part in the anhydride formation. On heating the tannin with zinc powder and 15% NaOH, resins were formed principally with a small amount of gallic acid and phloroglucinol. Dry distillation gave pyrogallol and traces of other phenols.

The Electrolytic Determination of Tannin. M. CORRIDI. *Collegium*, 1909, No. 371, pp. 281-3.—The author has tested the method of Metzges (abstr. this JOURNAL, III, 357) by precipitation through the continued action of an alternating current through Al electrodes. He finds that on addition of other colloids such as gum, dextrine, etc., these are thrown down in part with the tannin. Comparative analyses of various extracts gave higher results by the current than with hide-powder. It was found that 30 min. were insufficient to precipitate all the tannin, 1½ hrs. being required. The precipitate was gelatinous, filtering slowly and owing to the concentration of the liquid by the heat of the current, it was necessary to readjust the filtrate, before evaporation of an aliquot portion for non-tans. The author therefore thinks the process cannot replace the hide-powder method, although it may be useful in special cases.

Percentage of Tans:	Filter method	Invert current	Alternate current	Continuous current
Mimosa	39.54	40.51	40.37	40.60
Mimosa	39.57	41.19	41.29	40.93
Valonia	28.67	31.12	31.40	31.27
Valonia	28.64	30.58	31.09	30.29
Myrabolams	27.30	29.76	29.23	30.17
Myrabolams	27.92	30.15	29.40	29.86
Quebracho	33.31	37.32	35.77	36.90
Quebracho	32.95	36.60	35.40	35.86

Chrome Tanned Harness Leather. *Ledertechn Rundschau*, 1909, No. 28, pp. 220-1.—The main difficulties in the manufacture are more in the currying than the tannage. A smooth, handsome grain is desired which is not easily obtained in chrome leather. The leather must be curried in the moist state and then dried in frames to avoid wrinkling. Only a limited amount of fat can be taken up by chrome leather and is best applied in an emulsion liquor. The rendement by weight is lower than with vegetable tanned leather, so the product is sold by surface measure. Chrome harness leather is superior to vegetable tanned leather in tensile strength, sometimes double, with less stretching proportionally. It is also lighter; instead of 1.15, the specific gravity is from 0.8 to 0.95; a gravity of 1.0 indicates fault in manufacture, excess of mineral matter. Comparing further, the caoutchouc like nature of the chrome leather enables it to better resist friction and also to withstand chemical action in the stable. In wet weather, the amount of water absorbed and retained is less.

Soap Dressing on the Grain of Leather. *Ledertechn Rundschau*, 1909, No. 31, p. 243.—Ordinarily this dressing is only applied to the flesh but can be of use on the grain when this has been opened during tannage or the preceding treatment. A good recipe is:—4 lbs. grain soap, 1½ lbs. tallow, 30 to 50 gms. wax, boiled with 25 litres water and stirred till cold, this being essential. Another case is when the leather has had too little fat, having a light colored, more or less brittle grain. Here, liquid fat, whale or bone oil is added to the dressing according to need, amounting sometimes to half the soap. A good soap dressing may also replace more laborious and expensive finish in currying buffed leather.

The Prevention of Mold on Leather. L. MANSTETTEN. *Ledertechn Rundsch.*, 1909, Nos. 32-3, pp. 250, 258-9.—Above all, cleanliness of walls, floors and supports in the drying and storage rooms is important, these often being the original sources of the mold fungus. In many tanneries, the mold originates in old rinsing vats; these should not be over 1 m. deep, to hinder too long usage. Mold in storage rooms is best overcome by removing the leather temporarily and burning sulphur. If this cannot be done, dilute hydrofluoric acid sprinkled on the floor is very efficacious. Care must be taken in its use as the acid is very corrosive and its vapor attacks the breathing organs. The author has not had success with formalin. A solution of 0.05% sublimate is best for de-

stroying mold in hanging poles, covering cloths, etc., but the salt being unstable will not permanently prevent late growth. For this, sodium fluoride is best in 2% solution and may be used on leather. Only the completely soluble salt should be purchased, the sodium silicon fluoride being not nearly as antiseptic as sodium fluoride. Mold can also be transferred to the leather from oil casks. Before use, the oil should be heated and let cool. Salicylic acid dissolved in the oil will also arrest the evil.

Study of Tanning Extracts, (continued.) U. J. THUAU. *Le Cuir*, 1909, [2] No. 6, pp. 126-7.—In the preceding, it was pointed out that the non-tans as far as they fail to tan, are useless or even injurious to leather, making it permeable to water. They may play however another röle as tanning agents. The tans themselves break down on heating into gallic and ellagic acids, glucose and especially phlobaphenes or tannin anhydrides. These last under proper conditions can hydrolyze back into tannin. For instance, if a chestnut liquor be concentrated over direct fire, thereby decomposing a portion of the tannin, and then be detanned with hide-powder the filtrate after standing in the air for several months, will show additional tannin due to hydrolysis of the anhydrides. The determination of such non-tans as are capable of being transformed again into tannin would be a desirable problem for the chemist to solve and would apply especially in autoclave extraction. For vat tannage, well decolorized extracts containing little sugar and considerable non-tans, implying a manufacture under pressure and presence of notable amounts of phlobaphenes would be preferable to one of the same tannin strength containing less non-tans, for in the first case additional tans are formed in time. In drum tannage, there is not time for this change and extracts containing little non-tans are better.

School of Tanner, Plumping, (concluded.) A. SCHMIDT. *Le Cuir*, 1909, [2] Nos. 12, 14, pp. 267-9, 315-7.—The mineral acids sulphuric and hydrochloric have the advantage of cheapness and are much used for heavy leather. There is danger however of injury to the leather in time; of the two, sulphuric acid is the most persistently retained in spite of washing. In dilute solutions of equal strength (1 or 2 litres to 1,000). the hydrochloric acid plumps much more rapidly than the sulphuric which proceeds gradually. With more concentrated solutions the action of the two acids is nearer alike, but for the same amount of absorption, the hydrochloric acid produces more swelling and may be considered the most aggressive in attacking the leather.

Organic acids, such as acetic and lactic, are more expensive but have the advantage of acting gradually and the leather produced does not deteriorate on long storage and stands usage; of these acids, acetic plumps the least. The difference in cost between sulphuric and lactic acids is lessened by the circumstance that lactic acid has double the plumping effect for the same acidity. Oxalic acid, hitherto little em-

ployed because of its cost, has many advantages; its absorption is rapid without violent effect upon the leather, neither does the action greatly increase with the strength, so that an excessive plumping need not be feared. The plumping action of formic acid is more rapid than of lactic or oxalic acid, the relative increases of thickness of butt being 13.6: 5.5: 9.4%; it therefore needs to be used cautiously and then gives good results. It has the advantage of being antiseptic, preventing fermentation and saving tannin.

Even if the hides have been sufficiently plumped in a separate bath, it is faulty to proceed with the tannage in a liquor containing no acid, for the equilibrium being unbalanced the acid will leave the hide again which falls down. The best method is to plump the hide in the tan liquor itself with very gradual increase of acid, and subsequently to maintain the acid strength until the hide has taken on substance enough not to fall. In rapid tannage, it is essential to push the plumping to keep pace with the tanning, otherwise the interior of the hide is not fully tanned, a frequent defect with provincial tanners.

PATENTS.

Attachment to Leather Seasoning Machines. U. S. Patent No. 930,700. F. F. SLOCOMB, and W. E. POINSETTE, Wilmington, Delaware.

Process of Making Extracts. U. S. Patent No. 930,909. W. WIEGAND, Merseburg, Germany.

A process for extracting matter from solid material, which consists in advancing the material to be acted upon in one direction and continuously feeding a small quantity of water in the other direction to enable the solid material to stand at a higher level than the liquor, continuously drawing off the extracted liquor in one direction and discharging the solid material in the other, and stirring the material while feeding it in such a manner that the parts which lie beyond the level of the liquor are dipped into it and other parts raised out of it, whereby mixing of the strata of liquor of different degrees of concentration is prevented.

Putting-Out Machine. U. S. Patent No. 931,340. F. J. PERKINS, Woburn, Mass.

Means for Tanning and Depilating Hides and Skins. U. S. Patent No. 931,858. C. J. GLASEL, Boston, Mass.

A tanning drum having a detachable hide supporting frame, rotating with the drum; combined with this is a device independent of the movement of the drum, and which serves to stretch the supported hide.

Artificial Leather and Process of Making Same. U. S. Patent No. 933,645. L. V. GUILLETEAU-CHAPUT, Paris, France.

A process of making artificial leather, consisting in mixing balata gum in solution in toluene and water with dextrin, adding thereto a mixture of glycerin, sodium silicate and gelatin, combining with the mixture a fiber, kneading the mass to thoroughly incorporate the fiber therein, molding the mass into appropriate forms, drying the forms, passing the forms through a process, and finally subjecting the forms to a bath of formic aldehyde.

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W. H. TEAS . . . . . Editor and Manager

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IMPORTANT NOTICE.

The Secretary wishes to call especial attention to the ballots on the Proposed Changes in Methods, By-laws, and for Ordinary Members of the Council, which were sent out early in October. Every Active member, if he has not already done so, should send in his vote at once. As the ballots on the Proposed Changes in Methods and those for Ordinary Members of the Council require a *mail* vote, it is very important that every member give this his immediate attention.

H. C. REED,
Secretary.

October 18, 1909.

EDITORIAL.

Washington was selected as the meeting place for our Sixth Annual Convention, because the Council deemed it as convenient as any of the large cities, and also because our past experience has taught us that the best attended meetings have been held in Washington. We sincerely hope that the attendance will be in keeping with our past experience, and in view of the excellent program that has been arranged we expect to meet a large percentage of our associate membership.

In addition to the routine work on analytical methods which is of interest to our active members, many addresses by authoritative speakers have been arranged, and these addresses are to be on subjects which will be of interest to the practical tanners, leather merchants and others represented in our associate membership. We trust that these associate members will encourage the work of the Association by their presence, and we believe that their attendance will be with profit to themselves.

With the active members, presence at the annual meeting is a duty, and all members having the welfare of the Association and its work will be present, if their presence is possible. It will be the fault of the members themselves if they do not find our meetings sufficiently attractive to command their attendance.

To the younger active members we are impelled to say that the responsibility of the future welfare of the Association is on you; older men are constantly going from the laboratory to fields of applied science, and you must take their places in the experimental work of the Association. Come to the meeting and bring papers to read before the convention. Participate in the discussions and be really active members. Use the JOURNAL for publishing your observations of interesting and profitable experimental work, and do all you can to fit yourselves for the time when *you* will be the Association.

Let each of us make a really honest effort to be at Washington.

PROGRAM OF THE SIXTH ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

The sixth annual meeting of the American Leather Chemists

Association will be held at Washington, D. C., Dec. 2nd, 3rd and 4th, 1909, convening at 9.30 o'clock a. m., Thursday the 2nd.

The following order of business will be observed:—

THURSDAY MORNING.

President's Address.
Report of Secretary and Treasurer.
Committee Reports.

THURSDAY AFTERNOON.

Address by Mr. F. A. Vogel upon "English Methods of Tanning."
Address by Mr. C. M. Morrison upon "Extract Tannage."
Address by Mr. Oma Carr. (Subject deferred).

FRIDAY MORNING.

Committee Reports.

FRIDAY AFTERNOON.

Address by Mr. R. W. Griffith upon "Principles of Liming."
Address by Mr. C. M. Proctor upon "Bleaching of Leather."

SATURDAY MORNING.

Committee Reports.
Address by Mr. J. E. Stevens upon "Quebracho Development."

SATURDAY AFTERNOON.

Address by Dr. W. W. Stockberger upon "The Production of New Tanning Materials in the United States as an Agricultural Industry."

The Association has selected for its headquarters, the Raleigh Hotel, corner Pennsylvania Av. and 11th St., N. W.

The following are the rates for rooms:—

A single room without bath	$2.00 up
A single room with bath	3.00 up
Two in room without bath	3.00 up
Two in room with bath	4.00 up

Members who desire accommodations reserved are requested to communicate with the Secretary before Nov. 25th.

A room for the meeting has been secured at the Raleigh Hotel.

H. C. REED, *Secretary*.

LEATHER ANALYSIS.[1]

By F. P. Veitch.

On June 18, 1909, two samples of leather were mailed to those members of the leather committee who expressed a desire to receive them and the following instructions were sent with the samples.

INSTRUCTIONS FOR THE ANALYSIS OF LEATHER SAMPLES.

1. Make the extraction and all determinations as directed in the Official Methods of the American Leather Chemists Association (JOURNAL A. L. C. A., Vol. 4, page 124), except that in the determination of glucose for 20 cc. of lead subacetate use 20 cc. of neutral lead acetate and remove the lead from 400 cc. of the filtrate with a small excess of potassium oxalate. It has been definitely shown that the use of lead subacetate gives low results on sugars and it does not seem necessary for the Association to experiment on this point or to use a method which is known to give erroneous results.

2. Determine glucose as suggested by Veitch (JOUR. A. L. C. A., Vol. 3, p. 261). Treat 500 cc. of the water extract with 25 cc. of neutral lead acetate. Shake well, let stand for one hour and filter and treat with a small excess of potassium oxalate. Filter and to 420 cc. of the filtrate, add 5 cc. of HCl and boil down to 175-190 cc. and then for two hours with a reflux condenser cool, neutralize, filter if necessary and make up to 200 cc.

Treat an aliquot portion with Fehling solution in the usual manner, being careful to keep a total volume 145 cc. as specified.

3. Extract leather according to the following method:

Treat 15 grams of leather in some form of extractor that will allow the continuous percolation of liquid for 7 hours, at the same time keeping a volume of the percolated liquid within one liter, the extraction to be made at 50° C. The first 200 cc. should be collected in an outside flask without boiling, while the subsequent solution in the receiving flask is changed and combined with the first extract as concentration demands. Determine total solids, non-tannin, and glucose in this extract by the Asso-

[1] Report of the 1909 Committee.

ciation methods, except determining glucose as directed under 1.

4. Determine glucose by Allihn's modification of Fehling's method, Bulletin No. 107, Bureau of Chemistry, page 49.

Place 30 cc. of the copper solution, 30 cc. of the alkaline tartrate solution and 60 cc. of water in a beaker and heat to boiling. Add 25 cc. of the solution of the material to be examined, which must be so prepared as not to contain more than 0.250 gram of dextrose and boil for 20 minutes. Filter immediately through asbestos without diluting and obtain the weight of copper by the following method:

Prepare a Gooch with an asbestos felt one-quarter of an inch thick. Thoroughly wash the asbestos with water to remove small particles. Then follow successively with 10 cc. of alcohol and 10 cc. of ether, and dry the crucible and contents 30 minutes in a water oven at a temperature of boiling water. Collect the precipitated cuprous oxide on the felt as usual. Thoroughly wash with hot water, then with 10 cc. of alcohol, and finally with 10 cc. of ether. Dry the precipitate 30 minutes in a water oven at a temperature of boiling water, cool and weigh. The weight of cuprous oxide multiplied by 0.8883 gives the weight of metallic copper. The corresponding weight of dextrose is found through Allihn's table given in Bulletin No. 107.

Please report results of your work at the earliest possible moment so that I may present it to the Association in time for the forthcoming meeting. Give also your opinion on the relative value of cochineal, carminic acid and methyl orange as indicators in the determination of nitrogen, and on the most desirable way to report magnesium sulphate in leather, whether with or without the water of crystallization.

The samples sent out were marked No. 1 and No. 2. Sample marked No. 1 was an oak tanned leather, containing no added glucose or epsom salts, while No. 2 was another portion of No. 1 to which 8 per cent of glucose (actual) and 4 per cent. of $MgSO_4 + 7H_2O$ had been added.

Unfortunately no other member of the Committee on Leather Analysis has found time to report work to the chairman, nor to make any comment on the several subjects referred to the com-

mittee, except Dr. Hellon of England, who makes certain suggestions which are taken up later in this report. This report and the recommendations are, therefore, the work of my own laboratory and the recommendations are the conclusions drawn from much experimental work on the analysis of leathers. The results obtained are given in the following tables:—

RESULTS OF THE ANALYSIS OF LEATHER.

	Sample No. 1		Sample No. 2	
	Rogers	Stewart	Rogers	Stewart
	%	%	%	%
Moisture 15 hours at 98°	7.4	6.8	9.7	9.6
	7.4	7.0	9.6	9.6
Petroleum ether extract	5.7		4.3	
	5 7		4.3	
Ash	.3	.4	1.9	1.9
	.4	.3	1.9	1.9
Magnesium sulphate ($MgSO_4 + 2H_2O$)	0.	0.	4.0	4.0
	0.	0.	4.0	3.9
	14 hours extraction			
Water soluble at 60° as directed in instruction No. 3	16.5	16.1	26.4	29.4[1]
	16.7	15.6	27.6	29.4
Water soluble at 30° as directed in instruction No. 3	12.9		24.7	
	12.7		21.8	
Soluble non-tannin at 60°	3.2	3.2	15.1	15.4[1]
	3.2	2.8	15.7	15.7[1]
Soluble non-tannin at 30°	2.9		15.3	
	2.7		15.0	
Soluble tannin at 60°	13.2	12.9	11.3	14.3[1]
	13.5	12.8	11.9	10.6
Soluble tannin at 30°	10.0		9.4	
	10.0		6.8	
Soluble glucose at 60° as directed in instruction No. 4	.8	.7	8.2	8.1
	.7	.8	8.4	8.3[1]
Soluble glucose at 30° as directed in instruction No. 4	.8		8.5	
	.8		8.4	
Hide substance	37.3	37.3	31.1	31.1
Combined tannin (by difference)	32.7		28.1	

[1] 14 hours extraction.

Mr. Rogers obtained the following results on drying the samples for different periods at 98° C.

	Sample No. 1	Sample No. 2
Moisture dried 5 hours	7.0	9.2
	6.9	9.2
Moi ture dried 10 hours	7.0	9.3
	6.9	9.1
Moisture dried 15 hours	7.4	9.7
	7.4	9.6
Moisture dried 20 hours	7.4	9.7
	7.4	9.7
Moisture dried 25 hours	7.4	9.7
	7.4	9.7

These results indicate that 15 hours drying is required at 98° to secure constant weight on sole leather.

Sample No. 2, containing hydrated magnesium sulphate, did not take longer to dry than Sample No. 1.

Mr. Stewart obtained the following results on glucose in a comparison of basic and normal lead acetate as a clarifying agent:

	Normal lead acetate	Basic lead acetate
Sample No. 2	8.1	6.4
	8.2	6.2
1400	13.7	11.7
1405	.14	.16
2077	9.4	7.8
2114	8.3	6.5
2116	9.2	6.9

The results where the normal acetate was employed are much higher than those where the basic acetate was used.

No definite conclusions can be drawn from so few results. It may be said, however, that the results on moisture, ash, magnesium sulphate, and glucose are as consistent as can be expected. It is not probable that moisture can be determined as closely in all kinds of leather as has been done in these, nor is it likely that different workers will get closely agreeing results on ether soluble, as it is well known that both these constituents are very difficult to determine.

The results further indicate that glucose, when present, is quite easily extracted, as much being obtained in the extract at 30° as in that gotten at 60°.

The results on total water soluble and on tannins and non-tannins show wide differences, which the referee believes are to be attributed to the difficulty of extracting so large a quantity of material, and to differences in frequency of syphoning. Mr.

Rogers observed that where duplicate extractions did not proceed at the same rate the duplicates did not agree, and the slower extraction gave the lower result. It is essential, therefore, (particularly where the constituent determined is never completely extracted) that a definite number of syphonings be made in all cases. It is interesting to note that the differences in water solubles fall almost entirely on the soluble solids, the soluble non-tannins of the two analysts being quite constant at different extraction temperatures. It is not possible to extract the uncombined tannin without removing a small quantity of combined tannin, and these results show how difficult it is to determine the proper stopping point. The procedure, in any case, must be arbitrary, but our experiments indicate that the procedure outlined most accurately distinguishes between combined and uncombined tannin.

Indicators.—No work was called for with different indicators. It is the chairman's opinion that, provided standard indicators are used, the particular one which should be employed is entirely a question of individual preference and color vision. One precaution should always be observed: The same indicator should be employed in analysis that was used in standardizing the alkali. Cochineal, carminic acid and methyl orange are all suitable indicators. Dr. Hellon finds Rupps' methyl red excellent and strongly urges that it be included in a list of indicators suitable for use in nitrogen determinations.

Reporting Epsom Salts.—Dr. Hellon states that he always reports as "epsom salts" that is with the water of crystallization and this seems to me to be the only way to report it.

Recommendations.

Add to Section 4, provisional methods for leather analysis the following:—

Determination of Epsom Salts.—Dissolve the weighed ash in hot dilute HCl, add a slight excess of NH_4OH and ammonium oxalate to the hot solution, filter and wash. To the cold filtrate add slowly with constant stirring an excess of sodium phosphate solution, followed by 10 to 15 cc. NH_4OH. Allow to stand at least 3 hours, filter, wash free of chloride with 2½ per

cent NH_4OH, ignite, cool, and weigh. From the magnesium pyrophosphate found calculate the $MgSO_4 + 7H_2O$.

Change Section 5 to read:

Digest 15 grams of leather over night in a Soxhlet or other suitable apparatus, then extract with water at 50-55° C. for 7 hours. When the extraction has continued for about 2 hours, remove the extract from the receiving flask to a graduated liter flask. Continue the extraction with fresh water, using about 300 cc. each time, removing the extract and combining it with the first portion as concentration demands. (Three successive extractions each with 300 cc. water is recommended), make up to volume and determine total solids and non-tannins according to the official method for extract analysis.

Section 6 to read as follows:

To 200 cc. of the solution obtained as directed in Section 3, add 25 cc. of a saturated solution of neutral lead acetate. Shake well, let stand for one hour, filter and treat with a small excess of dry potassium oxalate. Filter and to 150 cc. of the filtrate add 5 cc. HCl, connect with a reflux condenser and boil for 2 hours. Neutralize, make up to 200 cc. and filter if necessary.

Place 30 cc. of Allihn's Fehlings copper solution, 30 cc. of alkaline tartrate solution, and 60 cc. of water in a beaker and heat to boiling. Add an aliquot of the glucose solution containing not more than 0.25 gram of sugar, dilute with water to 145 cc. if necessary, cover with a watch glass, bring to a boil and boil 2 minutes. Filter immediately without diluting through an asbestos mat in a Gooch crucible, wash with hot water to free from soluble salts, then with alcohol, and finally with ether, dry ½ hour in water oven, cool and weigh. Calculate to dextrose, using Allihn's table for the determination of dextrose. See Bulletin 107, Revised, Bureau of Chemistry.

To Section 7, paragraph "Indicators," add:—

Methyl orange may be used if preferred.

Work on the extraction with petroleum ether and on water solubles should be continued.

VACUUM EVAPORATION.[1]

By P. B. Sadtler.

It is a notable fact that, in this country at least, the knowledge of construction and operation of vacuum evaporating apparatus is very limited. There are a few industries, among which are the glucose, cane and beet-sugar industries, where the engineers are in general pretty thoroughly familiar with this subject. Outside of these industries ignorance of the basic principles of evaporation actually frequently prevents engineers and superintendents from obtaining the best results. Those operating vacuum apparatus in their plants are prone to drop the subject completely as soon as their apparatus has been "broken in," only to take up the subject again when something goes wrong or when increased capacity must be installed to meet the demands of a growing business. Besides this class there is a long, though gradually diminishing, list of factory owners and others who either have entirely neglected to consider this important subject, or who, on doing so, have been frightened by some obstacle that seemed unsurmountable.

In this article will be discussed only the form of evaporator in which saturated steam is the heating medium, as no evaporation can at present be done by direct fire so well as in the approved types of boiler, where the steam for the evaporator is made. The reasons why direct fire evaporation does not as a rule pay will be discussed on a later page.

A closed evaporator heated by steam coils has the following advantages:

1. Less steam is used because the apparatus is smaller and there is no exposed surface of boiling liquid, hence the amount of radiation and consequent loss of heat is reduced.

2. When evaporating under vacuum the temperature of the system is so lowered as to be nearly down to that of the atmosphere, with the result that the radiation loss is decreased. In other words, if a liquid is boiled in an open pan under atmospheric conditions the boiling point may be 220° F., or 150° above average atmospheric temperature. In a single-effect vacuum evaporator the average temperature may be 138° or 68° above

[1] From the *Journal of Industrial and Engineering Chemistry.*

atmospheric temperature. The radiation from the open pan would compare with that of the vacuum pan as 150° to 68° roughly.

3. The above considerations, however, are of little importance compared with the fact that a vacuum evapoprator, either single- or multiple-effect, may be run by using, as a heating substance, the *exhaust steam* from engines, pumps, etc., thus enabling certain establishments to run an evaporator at practically no cost for steam.

4. There are many liquids which should be kept below the temperature 280° to 300° of high pressure steam coils, or even below atmospheric boiling point 212° F. Among these are such as sugar, glucose, sugar of milk, milk, glue, glycerine, etc.

5. Greater temperature differences may be attained in single effects, hence greater capacity for a given size apparatus.

6. When multiple-effect evaporators are used, the steam economy is increased to such an extent as to make the steam consumption run as low as ⅕, in some cases, of the actual amount of water evaporated from the liquid. There are some industrial concerns at present which could not operate and pay dividends without multiple-effect evaporators in constant use.

Multiple-Effect Principle.

The most primitive illustration of a multiple-effect evaporator is seen in an organic laboratory every day. Frequently a so-called volatile substance is put into a flask connected to a condenser and heated by a steam bath in which water is boiled. The vessel containing the boiling water is the first effect of a double-deck evaporator and the flask containing the low-boiling substance is the second effect. In the case of large scale work instead of boiling off a naturally volatile substance in the second effect, we boil off water whose vapor above it is kept at reduced pressure, thus making the water a relatively low-boiling substance. Thus in practice we have a succession of pans or effects, the coils of each one of which gets its heating vapor from the liquid of the preceding pan. The first pan of the series takes its heating vapor from the original source, the boiler or exhaust pipe of an engine; the last effect gives up its vapor to a condenser in which the highest vacuum is main-

tained. Any important point to be borne in mind is, that every effect is the condenser that brings about the pressure reduction necessary for the operation of the preceding pan.

The most popular and universally serviceable evaporator is the triple-effect, although they are in daily operation on a large scale up to sextuple-effect. In fact, multiple-effect water stills have been operated in twelve successive effects. A definite determination of the number of effects to use to obtain the best economy when working on any given solution, is difficult to make. The best tests, of course, are those made on the large evaporators and as some expense and annoyance to the owner may result, the proper scientifically conducted tests are not carried out. One can, therefore, only go by the judgment of the designers and experts in this field in determining the best layout for economical multiple-effect evaporation.

Steam Consumption.

Before discussing at length the factors governing the steam consumption in an evaporator, it is well to state several fundamental facts to be proven later.

1. *The number of effects used in an evaporative system does not necessarily bear any relation to the evaporative capacity of the system.*

2. *A given amount of water at the boiling point to be evaporated requires a corresponding amount of steam to evaporate it irrespective of the form or size of the vessel in which the evaporation is accomplished. Speaking broadly, a pound of water* evaporated requires that a pound of steam be condensed in a single effect.

3. *The capacity of a heating surface is dependent on the temperature of the steam and not the pressure resulting therefrom.*

4. *An evaporator should not be considered as a heat engine, as it does no external work.*

To get the best idea of the heat transactions in the evaporator, we should consider one effect at a time. Also, for simplicity, assume that the effects are of the same construction and bear in mind that each one is the condenser to produce the vacuum in the preceding effect. For every pound of dry steam entering the coils of the first effect, there is one pound of vapor produced

by the evaporation of the solution which we assume enters at the boiling temperature. As only a fraction of the total amount of water is to be evaporated in the first effect, the solution passes partly concentrated into the next effect. But as a lower pressure, and consequently lower temperature, is being maintained in the second effect, the solution passes in a superheated condition to the next effect, where a certain amount of evaporation takes place, due to the lowering of the pressure. Therefore in the second effect we have to expect the evaporation of another pound, plus increment due to the changing part of the heat of the liquid into heat of vaporization. Likewise in the third effect there is produced evaporation to the extent of a pound, plus two increments. In other words, the latent heat of a pound of steam is transferred through the heating surfaces of one effect after another, the amount of steam being, however, gradually increased by the spontaneous evaporation of the solution passing from one effect to another successively in a superheated condition. Finally this heat passes into the cooling water of the condenser and is lost. If we were to assume that there was no radiation of heat from the system and that pure water were being boiled, the above conditions would be always true and, in a sextuple effect, a single pound of initial heating steam would accomplish the evaporation of between six and seven pounds of water.

In actual fact, however, we have to contend with the consumption of heat in two other directions:

1. In concentrating any solution we have to accomplish the partial separation of a liquid from a solid. There is, of course, a certain solution pressure against which we must work, and the actual amount of energy expended in this way is measured by the free energy of the chemical reaction of solution. This is not considerable when we concentrate to ordinary density. Hence it may be said that *the total reversible energy expended in evaporation is equal to the free energy of reaction.*

2. There is a radiation loss from each effect depending on the number of effects, their temperature with respect to atmospheric temperature, the amount and quality of the insulating covering used and other conditions such as degree of exposure of the apparatus to the weather.

These losses are cumulative from one effect to another so that where a solution has boiling points appreciably over that of water, it is not economical to attempt the operation of more than a limited number of effects.

Diagrams.

To illustrate several cases of heat transactions obtaining in an evaporator:

Figure 1 shows a multiple-effect heat diagram similar to that of Hausbrand for pure water in a quadruple-effect evaporator, where it is assumed that the difference in temperature from one

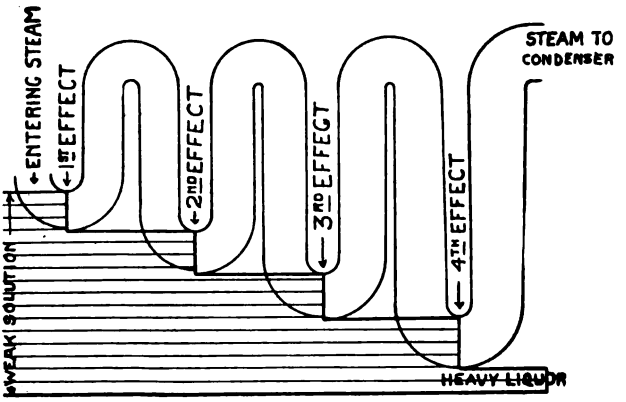

Fig. 1.

effect to another is infinitesimal and where water enters at boiling temperature and the vessels do not radiate heat.

Figure 2 shows a heat diagram for a triple-effect where the assumptions are made that the solutions enters at atmospheric temperature, the solution has an appreciable excess in boiling temperature over that of water, and there is an appreciable temperature difference from one effect to another. The white areas represent the steam condensing and causing evaporation; the shaded areas represent the heat and energy losses as expressed in steam. The areas shown are not definitely measurable or calculable, but merely in the diagram show the tendencies existing in an evaporation system.

The heat transferences taking place in a multiple effect are altered in character to a great extent by the method of feeding

the solution to be concentrated and the method of preheating if such is necessary. There are four ways of feeding the solution to the evaporator.

1. The dilute solution is fed entirely into the first effect and passes successively from one effect to another at higher and higher concentrations.

2. The dilute solution is fed in equal amounts separately into each effect, and boiled in each at the same concentration.

3. The dilute solution is fed entirely into the last effect and passes back to the first effect, a method known as running backward.

4. The dilute solution is pumped into the whole evaporator before starting and boiled in batches.

While inquiring into the relation, merits and advantages of these

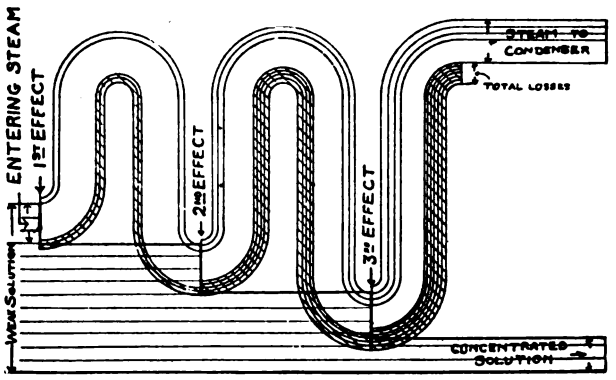

Fig. 2.

methods, let us consider at the same time the methods of bringing the dilute liquor to the boiling point and the bearing of these methods upon the heat transactions.

While in many cases a recently completed chemical reaction or industrial process leaves the dilute solution at a temperature approaching the boiling point, such as we find to be the case in certain mercerizing work, in electrolytic soda work or packing house rendering, there are other cases such as brine evaporation or sugar evaporation where the most efficient process necessarily includes the preheating of dilute solutions. In general, it may be said that running a comparatively cool solution

into an evaporating apparatus decreases its efficiency and interferes with proper operation.

The usual method of preheating in running a multiple-effect concentrating evaporator as mentioned, in case 1, above, is to employ a steam heater to preheat the solution entering the first effect by the use of live or exhaust steam. Frequently it is assumed that it is quite sufficient to turn on a little extra steam and run the solution cold into the evaporator. When this is done a portion of the heating surface of the effect, into which the cold solution is run, plays the part of a preheating apparatus. An evaporator is an expensive article to use as a preheater.

Where evaporating at equal densities, as in the second case above, there may be attached to each effect a countercurrent heater in which the water of condensation, flowing from an effect, partly preheats the liquor being pumped into the effect. It can readily be perceived that the amount of heat that can be transferred to the solution from the water of condensation is insufficient to bring the former up to the required boiling point. This method is only applicable to precipitation work, as in multiple-effect salt evaporators.

When "running backwards" preheating is not often the practice as the boiling point of the last pan, the one which the solution enters, is not very high and the step up in temperature from one pan to another is not very great. This method has the advantage, but other things being equal, that in the pan with the densest solution, there is the highest temperature, which tends towards better circulation and consequently higher efficiency. In using this method it is necessary to pump the liquid out of one effect into the next. The fact that steam is used to do pumping need not have much bearing on the question, as it must be borne in mind that the exhaust steam from pumps is available for evaporation purposes.

The total consumption of heat in a multiple-effect is composed of the energy consumed in actual separation of the liquid and the solid in solution; the radiation of heat from the walls of the vessel; the heat passing away in the circulating water of the condenser; and the heat passing away in the condensation water. In a test on an evaporator these can all be determined by actual measurement except the energy of evaporation and the radiation

loss. There is always considerable doubt as to just what the latter amounts to in various types of evaporator and with various coverings. It is possible to measure it by special test, though this is rarely done. The energy of evaporation may be calculated for certain solutions and simply depends on a formula which may be derived from the gas laws.

It is shown by Nernst in the last edition of his "Theoretical Chemistry" that the energy expended in evaporation is

$$K \times R \times T \times (C—C'),$$

where R = the gas constant, T = the absolute temperature, C′ = initial concentration, and C = the final concentration both expressed in mols. of salt per mol. of water. K is a constant quantity for any given substance in solution. For certain inorganic salts these constants have been determined, being derivable from the vapor pressure curves.

Efficiency and Evaporative Capacity.

A heat engine is an apparatus that transforms a portion of the heat received into dynamic energy. An evaporator is not a heat engine, therefore, but if the assumption be correct that solution is a chemical combination of solvent and solute, an evaporator transforms heat into chemical energy. When following this analogy between a heat engine and an evaporating system, we find that as a matter of fact the efficiency or the quantity $\frac{Q-Q'}{Q}$, where Q is the heat entering and Q − Q′ is the heat transformed in chemical energy, is very low. The heat disposed of through other channels is very great. For instance, the latent heat of the entering steam eventually finds its way in large part into the circulating water of the condenser. Therefore, it will readily be seen that if, as we have shown above, this energy demanded for evaporation is entirely dependent upon absolute temperature and degree of concentration, *no high type of evaporator has more efficiency than another, but the efficiency is entirely dependent upon the solution and its attendant physical conditions.*

This matter of efficiency is noted here as there is an erroneous conception among some evaporator engineers as to the meaning of the word efficiency. It has been the practice among some

to speak of the relative amount of evaporation per unit area of heating surface as the efficiency of an evaporator. The difficulty with using the term efficiency where the term capacity or duty would be more applicable, is that it leads those unacquainted with the principles to the idea that greater or less consumption of heat obtains in different types of evaporators. In different types of evaporators the evaporative capacity does vary considerably, but it is not the purpose of this article to discuss this side of the question, as the relative merits and demerits of different makes of machinery demand a separate article.

Before discussing the subject of capacity and the calculation of heating surface, it is well to approach the subject from the point of view of transmission of heat through the heating surface.

Heat Transmission.

Heat transmission is measured by four fundamental factors, namely, temperature, weight, space, and time. To be more specific, the common combination of units, in which we express heat transmission, is British thermal units, per square foot, per hour. Therefore, the coefficient of the heat transmission of a medium would be the figure which gives the number of British thermal units passing per hour from a warmer to a colder substance through one square foot of the medium for which we desire the coefficient.

It will readily be seen that the ability of the medium to transmit heat in a greater or less degree is governed by the following factors, namely, nature of the material, thickness of the medium, difference in temperature of the warmer and the colder substance. Hence, we have

$$h = k\frac{(t - t')}{d}m,$$

where h is heat transmitted, m is the time during which transmission takes place, d the thickness of the transmitting medium, $t—t'$ difference in temperature, and k a constant dependent on the nature of the material.

From the above we see that

$$k = \frac{d \times h}{(t - t')m},$$

whence we are able to determine a constant k for any material

by determining d, h, $(t—t')$, and m for one square foot of heating surface. For practical purposes, where for a given material the limits of the factor d are quite narrow, this is omitted and the constant becomes

$$k = \frac{h}{(t - t')m}.$$

In the case of the transference of heat from one substance to another, for evaporative purposes, we have several possibilities: that of heat passing *from* a liquid, *from* steam or *from* other gases; also heat passing *to* a body of liquid or *to* a film of liquid.

In evaporation work the case of heat passing from a liquid is not of very wide importance. Other things being equal k would be high in this case, but the difficulties involved in this method of heating necessarily outweigh those of steam heating. A high-boiling liquid may be heated and made to pass through heating tubes, giving a high transference constant, but the velocity necessary for its passage through the tubes is great enough to make the idea unworthy of consideration.

In the case of saturated steam there is not the same necessity for an appreciable velocity directly in relation with the walls of the heating tubes, though this is very desirable. Unlike the case of direct heating, the effect is obtained by the latent heat of vaporization. Although the heating of the liquid is not due to difference in temperature between the steam and the liquid being heated, there must be a quite appreciable difference in temperature to make effective use of the latent heat The larger the difference in temperature the greater is the heat transmission of the metal walls.

As water dissolves air to a small extent the steam from the boiler always contains air in greater or less amount. This air tends to lessen the heat transmission so that it will be found in practice that better boiling takes place in the heating coil, where the velocity is considerable.

It can readily be seen, therefore, that the presence of *air in the heating steam is detrimental.* Just as air reduces the heat transmission so also does the water produced by condensation of the steam. The heat conductivity of water is far below that

of a metal, so that a *steam coil containing a layer of water is not fully effective.*

The usual case of heating by other gases than steam is direct firing of boilers or evaporators, or the utilization of waste heat from furnaces, incinerators, etc. Here the transmission of heat is due to the difference in temperature and *the velocity of the gas.* It will readily be seen that if a body of cooled inert, non-condensable gas stays in contact with the wall of the heating surface the efficiency of the locality where that takes place is greatly reduced. On the other hand, in the case of steam the pressure back of the heating steam is cause for constant supply of the steam, which gives up its latent heat to the wall of the heating surface. A non-condensable gas, to be equivalent in effect to a condensable gas, like steam, must be led against the heat-transferring wall with considerable velocity to cause the rapid removal of cooled gas and prevent lodging of cooled gas in any small corners or devious places.

Very little can be determined as to the theoretical side of the transmission of heat *to* different solutions and solids. In general, it may be said that the completeness of the circulation of the liquid, the consequent rapidity of the disposal of the steam formed at the contact between the liquid and the heating surface, and the degree of mobility of the liquor are the chief factors for consideration here. More can be said later of interest and of value from a practical standpoint.

The heat transmission may be said to be greater when the liquid is in contact with the heating surface in as thin layers as possible. This is accomplished by allowing the liquor to spray or trickle over the heating surface or by bringing the liquor in contact with the surface in the form of a foam. When a film is in contact with the heating surface the evaporation may be said to be local; hence there is a local cooling tendency and consequent greater temperature difference between the liquor heated and the heating gas. This it will be seen will increase the heat transmission.

There has been an erroneous notion prevalent among some engineers that the evaporative capacity of a heating surface of any given form and area is inversely proportional to the thick-

ness of the wall of the heating tube and proportional to the heat conductivity of the particular metal used. The idea is quite wide of the mark, as decided by results. If two otherwise equal evaporators be installed in which one has heating tubes of 20-gauge and the other 15-gauge, such a theory would require that the latter would have half the evaporative capacity of the former, 15-gauge being twice as thick as 20-gauge. As a matter of fact the difference due to this variation in thickness is negligible. However, the difference between the evaporative capacities of two heating surfaces of different metals is measurable if two metals of widely different conductivities be chosen, but even then the difference is not great as might be supposed.

Kent gives, among others, the following conductivities:

Silver	1000
Copper (rolled)	845
Iron (wrought)	436
Steel	397

In spite of these figures the evaporative factor of copper tubes is only 10 per cent. to 15 per cent. greater than that of steel tubes.

To explain these facts we must consider that the resistances of the metallic wall to the passage of heat are threefold, namely, (1) resistance of entry of heat into the metallic wall, (2) resistance to passage through the wall, (3) resistance to the exit from the metal to the boiling solution. Let these resistances produce conductivities *a*, *b*, and *d*, respectively. Let C represent the evaporative factor of the metal by experiment.

$\frac{1}{C}$ = total resistance $= K\left[\frac{1}{a} + \frac{1}{b} + \frac{1}{d}\right]$ or the sum of the three resistances.

$$C = \frac{1}{K\left[\frac{1}{a} + \frac{1}{b} + \frac{1}{d}\right]}$$ where K is an arbitrary constant.

Conductivity is effected by the ease with which the steam for heating is carried off and also the velocity of the steam; conductivity *b* is constant for a given metal; conductivity *d* is dependent upon the solution being handled, its boiling point, mobility, scaling properties, etc.

Calculation for Heating Surfaces.

The amount of heating surface necessary in an evaporator to be used for any given class of work depends on the following factors: 1. The amount of water to be evaporated, (2) the number of effects desired, (3) the initial steam pressure, (4) the boiling points of the solution to be evaporated, (5) the evaporative factor for a given type of machine, and for a given solution to be evaporated.

In calculating the amount of water to be evaporated, it is merely necessary to obtain from tables or analysis, the per cent. of solids in the dilute and the concentrated liquor. From this we can obtain the amount of water to be evaporated. When

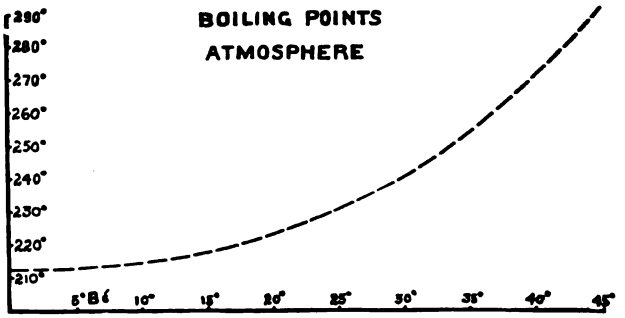

Fig. 3.

the number of effects in which the evaporation is to be done is determined, a calculation should be made of the water evaporated in each effect and from that, what the concentration should be maintained at, in each effect. When these concentrations are known the corresponding boiling points should be found from a good table of boiling points or by experiment, or a curve such as shown in Fig. 3 for certain grades of caustic soda washings may be used. The *degrees of excess boiling* temperature is the total of each of these boiling points less 212° F. In other words, if the boiling points in three effects of a triple effect are respectively 214°, 220°, and 236°, the excess boiling temperature is (214—212) + (220—212) + (236—212) = 34°.

From the steam tables of pressure and temperature the *total temperature range* should be found. Or it will be found very

useful to use a curve as shown in Fig. 4 where the pressures and temperatures are plotted. Readings from such a plot compare favorably in accuracy with actual steam gauge readings on the evaporator. This temperature gauge then equals the temperature corresponding to initial steam pressure corresponding to vacuum maintained in the last effect.

The *evaporative factor* is a constant quantity. The total temperature range less the excess boiling is the *effective range*. This divided by the number of effects equals the *average effect difference*. The evaporative factor is derived from experience

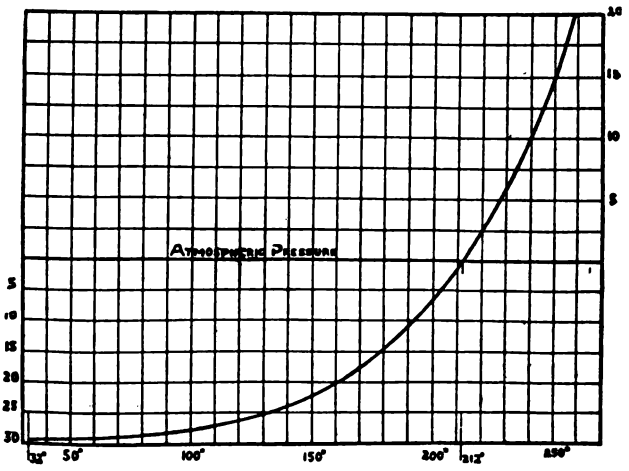

Fig. 4.

and from operative tests on the type of apparatus best adapted and on the given class of liquor to be evaporated. Probably the same factor would hold, for instance, on all submerged tube evaporators of the general type of those under discussion and would hold for either caustic soda solutions or carbonate of soda solutions, scaling conditions, etc., being otherwise the same. In fact the same constant quantity could be used, and has been used, in designing evaporators for a large range of inorganic chemical solutions, such as sodium chloride, sodium hydrate, sodium carbonate, sodium sulphate, sodium phosphate, sodium acid phosphate, sodium thiosulphate, potassium chloride, potassium hydrate, ferrous sulphate, calcium acetate, etc. However,

in cases of tannic acid, sugar, glucose, glycerine, black liquor, or resinate of soda, packing-house tank water, garbage tank water, etc., somewhat different conditions obtain and the factor varies. The factor also differs slightly for different materials for the heating surface, that for copper or aluminum being distinctly higher than that for iron.

To specify the units on which this factor is generally based we might say that it is expressed as gallons of water evaporated per square foot of heating surface per degree difference in temperature per hour.

If C = evaporated factor,
E = average effect difference,
W = gallons evaporated,
T = time in hours during which evaporation proceeds,
S = square feet of heating surface,

$$C = \frac{W}{E \times T \times S}.$$

Hence, if we find from experience or trial tests the value of C and we calculate E and W, as explained above, it is easy to obtain the required heating surface.

The successful designing of an evaporator is dependent first on the recognition of certain chemical and physical facts relating to the substance to be evaporated; second, on whether or not due regard is paid to certain thermal and thermo-dynamic principles involved; and third, on certain mechanical features that arise in the construction. It is not to be supposed that either an engineer, familiar with the best boiler practice, or a chemist, familiar with laboratory or open-pan evaporation in the works, could successfully design a multiple-effect evaporator. But certain facts in regard to design should certainly aid either a chemist or engineer in procuring the proper design or making a purchase.

As the principal purpose of an evaporator is to concentrate a solution of some sort, it will be readily seen that the chemical and physical laws governing concentrated solutions will be of importance. These are only known qualitatively and the quantitative laws which govern the chemistry of dilute solutions are inapplicable.

As most measurements of the concentration of solutions in the works are made with a hydrometer we generally speak of concentrating between certain limits in degrees, Baumé, Twaddell, Brix, salinometer, or specific gravity. It is, therefore, necessary to obtain or devise tables or curves showing the relation of these units of concentration with the percentage of solid matter in solution. The purpose of this is to obtain accurate information as to the actual amount of water that is going to be evaporated in a unit of time. This is especially important in cases where the vapor arising from the solution is the source of heat in the succeeding effect of the evaporator.

Of equal or greater importance, is a table or curve for a given solution which shall accurately show the relation between the boiling point of the solution and its concentration. It has been shown above, that the boiling point of a solution at any period of its progress through the evaporator has a direct bearing upon the size of the evaporator. A boiling point curve is generally obtained by taking simultaneous readings upon a hydrometer and thermometer, while boiling a solution actively under atmospheric conditions. This may best be accomplished in a laboratory where accurate means of determination are provided. After this curve is obtained a correction should be made for temperature at boiling to bring the hydrometer readings to the same temperature standard.

In cases where a substance is intended to precipitate from solution, during the process of evaporation, there should be used in conjunction with the above table also a table of solubilities of the substance at different temperatures.

The thermodynamic data necessary consist of the regular steam engineer's tables, showing the relations between temperature, pressure, heat of liquid, heat of vaporization, etc.

There are other chemical and physical data of which account must be taken in designing. The more information obtainable in regard to possible incrustation and scaling of heating surface, the clearer will be the idea as to what mechanical features to introduce for the removal of scale and as to what excess capacity to allow for this contingency. As in boiler practice, one of the greatest sources of annoyance is the deposition of gypsum

on the tubes. This annoyance is encountered in the salt industry especially; on account of the peculiar solubility relation of gypsum, it is found more expedient to evaporate at low temperature with large heating surface, thus minimizing the scale. Another similar case is that of soda washings in pulp mills, where cooking liquor is evaporated for soda recovery. If the lime used in the course of the process is high in silica and alumina, these find their way to the evaporator and deposit in a dense fibrous scale. If such possibilities as these are to arise, it is found expedient to have the heating surface in excess of the calculated area and easily removable from the evaporator for cleaning purposes. Moreover, it should be removable where corrosion is expected. There are some chemical solutions which corrode iron at the higher temperatures but are inactive at lower temperatures. In these cases the heating surface bears the brunt of the destruction in the evaporator.

Another important question is, as to the nature of a solution's activity under boiling conditions. In other words, does the boiling solution tend toward entrainment or foaming, or spattering? These points must be known beforehand, as they decidedly influence the proportioning of the evaporator.

Properties of Liquids as Affecting Construction.

In some industries the multiple-effect evaporator is among the largest and most expensive of the installations in the factory. Where a large evaporator is to be built for constant use, great attention should be paid to details of its design and construction. The liquids commonly evaporated in any quantity can be divided into two classes: those that foam on boiling and those that do not. It may be said in general that a liquor that entrains (or sprays and passes over with its vapor) does not foam, and a foaming liquor does not entrain. Also it is noticeable that solutions of alkaline reaction tend to foam while those of acid reaction tend to entrain. Most sugar juices and glucose come under the latter class. To provide against losses due to entrainment in an evaporator there are to be mentioned such methods as the use of baffle plates, catchalls, and high-vapor dome. The so-called film evaporators are subject to the difficulty in this respect that the vapor space allowed is invariably

small and from the time a portion of the vapor leaves the boiling solution it carries with it a large amount of spray in suspension in its rapid passage through tortuous channels of small cross-section. The simpler types of evaporator whose construction is more like that of a tank are open to the objection often, that the vapor is drawn off from a dome directly over the boiling surface. In these simpler types of evaporators it can be arranged easily to have the sectional area large enough to make the rising of the vapor slow and the height of the dome sufficient to cause practically all the entrainment to drop back. In order not to cause any inversion or possible discoloration in the sugar juices it has been found advisable to have as little as possible of the juice in actual transit through the apparatus. This is accomplished by two principal methods: one by having a rather shallow bank of tubes in which the tubes are packed in the tube sheets as closely together as possible; another by spraying the juice over the heating surface, collecting it underneath and pumping it back again to the spray. This latter method rather subjects the juice to loss from entrainment, unless the vapor dome is extremely high.

In dealing with soda solutions the problems arising are of a very different nature from those in sugar work. Under the head of soda solutions we may include, among other important cases, the evaporation of sodium carbonate, sodium phosphate, pure caustic soda and caustic soda containing brine (electrolytic), black liquor (pulp-mill), mercerizing soda, etc. Except in the case of the more concentrated liquor of the last effect these are all more or less foamy when boiling. The use of baffle plates alone does not accomplish the prevention of loss when foaming takes place. It has been found that the only sure and efficient way to deal with foam, that is to cause it to subside, is to break the individual bubbles by application of heat. Hence the evaporator should be built in such a way that the heating surface is in a high bank above the level of the liquor evaporating. On operating the apparatus it may easily be found by trial what is the proper level of liquid shown in the gauge glass to prevent the foam from rising much above the top of the tubes and yet keep the tubes covered. About

the most difficult liquors to handle in this respect are those in pulp-mills or mercerizing plants. In these cases it is necessary to have the heating tube bank almost half the height of the evaporator.

In salt industries there are two main difficulties which have to be met by the designer of an evaporator: first, the salt has to be removed from the apparatus constantly as it precipitates from solution; second, scale that deposits upon the heating surface has to be removed periodically. In order to render the removal of precipitated salt simple and rapid it has been found best to construct the evaporator with a hopper-shaped bottom having either one or two hoppers leading through a valve at their lowest point into a receiver where the salt is separated by draining through a false bottom. Another method consists in precipitating the salt continuously down a barometric leg under the evaporator, draining it and conveying it from the bottom by a closed elevator. This latter method is generally most efficient when working on a very large scale. In salt evaporation work, shut-downs are frequently necessary every day because of the constant deposit of gypsum upon the heating surface. This happens to such an extent that the evaporative capacity of the apparatus is reduced to a point where it no longer pays to operate. Ready means of access should be provided so that the heating surface may be thoroughly cleaned, or arrangements should be made for rapid pumping and boiling of suitable chemicals for the disintegration of scale.

There are certain acid salts which require special construction in order to line the evaporator with lead. This lead lining has never been done on a very large scale. In principle it consists in first pickling in sulphuric acid the plates of the machine, these being built with flanges that can be bolted together. The pickled surface is then given a tin coating. A sheet of lead of the proper thickness and size is coated with tin. The two tinned surfaces are laid together and the lead hammered to fit. Then the lead is "sweated" on by heating the iron from the outside to the melting point of the tin plating, which is lower than that of the lead. In this way the lead lining becomes attached to the steel by a homogeneous weld. Where the flanges

are bolted together the contact of the two lead surfaces generally prevents leakage, but can be made more sure by the process of lead-burning.

It is generally most expedient to work out the size of the heating bank from the amount of heating surface determined upon before deciding upon the general dimensions of the shell of the evaporator. The first thing to consider is the bore of tubing to be used. If we are dealing with a vertical type of evaporator where the tubes are expanded into two horizontal tube sheets, the bore of the tubing is determined by the nature of the liquid which is to be evaporated in them and the magnitude of the work to be accomplished. In the case of the horizontal type of evaporator where the steam is in the inside of the tubes and the liquor on the outside, there has been found a ratio of length to diameter for which the steam that condenses within gives a maximum evaporative capacity. If the tubes are too long and constricted, the steam will condense before it can pass to the far end of them, and a certain amount of heating surface is thereby wasted. It is usual to decide upon a certain length and diameter of tubing, however, arbitrarily from experience. It is then easy to decide, from the nature of the solution and taking into account the temperature differences and rate of evaporation, the proportioning of the heating bank. In a vertical effect when the length, diameter and center line distances are decided it is merely a question of filling a certain number of tubes in the minimum-sized circle.

Tubes may be attached to the tube heads or tube sheets by one of two methods, that of packing them in or expanding them in. To pack the tube in the tube sheet well, the hole in the sheet must be countersunk conically to admit of the forcing in of the rubber packing. This rubber ring is pressed in by a metallic place so that it is forced against the hole in the tube sheet by a stud bolt, and is arranged to hold down four, six or eight packing rings simultaneously.

When tubes are expanded into the tube sheet, it is expected that they are to be removed at no time during their life, whereas packed tubes can be easily removed, cleaned and repacked. Tubes expanded into the tube sheets properly make a perfectly steam-

tight joint for almost any pressure or vacuum. The tubes are extended through the sheets a slight distance and are beaded over and are expanded by a special tool for this purpose. The Prosser expander rolls a corrugation in the tube, just inside of the sheet and beads it outside the sheet. In this way the sheet is braced against pressure from within or without. The Dudgeon expander rolls the tube flat against the side of the hole and beads it over on the outside. This method is not as effective in results, but is less of a strain on the metal of the tube.

I hope at a later date it may be possible to go more deeply into the practical side of this subject, presenting as far as possible the best solutions to problems arising from day to day.

ABSTRACTS.

Trial of Zeuthen's Method for Tannin Determination. J. PAESSLER. *Collegium,* 1909, No. 374, pp. 305-12. This process (abstract, this JOURNAL III, 1908, p. 395) has the advantage over the official method in quantitative precision, since the hide-powder for each determination is weighed and washed separately; moreover the manipulation is simpler. It has been shown by the German Analysis Commission that ready chromed hide gives the same results as the official white. To depart as little as possible from the official method, the author uses the equivalent of 6.5 gms. dried hide-powder instead of 5.5 gms. as Zeuthen proposes. By selecting the larger filter bells, it is possible to use this amount. A specially made suitable size was 3 cm. diameter, 8.5 cm. high to the beginning of the contraction. It was found that the increased dilution to 35 gms. water used by Zeuthen does not affect the results, but it may be kept down to 20 gms. by use of a filter pump. Tabulated results (here condensed) are given of recent trials of the process at the Freiberg Station.

PERCENTAGE OF NON-TANS.

	Official method	Zeuthen's method 35 cc.	Zeuthen's method 20 cc.
1. Quebracho wood	3.15	3.0	2.75
2. Pine extract	15.6	14.45	15.6
3. Chestnut extract	13.3	13.9	14.0
4. Quebracho extract	6.4	6.25	6.5
5. Oak bark	2.65	2.45	2.6
6. " "	7.45	6.8	6.75
7. Pine bark	9.45	9.05	8.0
8. Valonia	14.4	13.1	13.05
9. "	15.0	14.2	13.8
10. Trillo	16.6	15.95	16.45

PERCENTAGE OF NON-TANS.—(*Continued.*)

	Official method	Zeuthen's method 35 cc.	Zeuthen's method 20 cc.
11. Myrabolams, shells	23.5	23.1	21.75
12. Mallet bark	12.4	12.1	11.75
13. Sumach	17.25	16.5	16.5
14. "	18.0	17.35	17.55
15. Lentiscus leaves	19.4	18.7	19.45
16. Oak wood extract	15.35	15.35	15.25
17. Chestnut wood extract	14.9	14.5	14.4
18. " " "	11.0	11.3	11.4
19. " " "	12.0	13.0	12.25
20. " " "	10.4	9.85	9.65
21. Quebracho Extracts, solid	6.0	5.8	5.5
22. " " "	9.6	8.9	8 9
23. " " "	6.8	6.4	6.65
24. Sumac extract	29.1	28.8	28.75
Average	12.9	12.5	12.5

In these determinations, 6.5 gms. hide were used except in the first 4, when 5.5 gms. were used in Zeuthen's method. It is seen that the smallness of the charge does not affect the result. Results are also tabulated of 57 double analyses both by the shake and Zeuthen's method (20 cc.). The averages of all were 12.15 and 12.06% non-tans, the individual differences being about equally + and —. A series of determinations with hide-powder of various preparations gave uniform results. In some cases, especially in warm weather, it was found that a washing of 30 cc. was insufficient; a washing of 50-60 cc. is therefore believed to be best when employing Zeuthen's method. A series of 10 test analyses thus carried out checked well. (14.1% official, 14.0% Zeuthen). Although the experiments made in the station as reported by the Commission showed that ready chromed hide-powder remains permanent on storage, many have objected to its use, claiming that the permanence did not hold good towards treated extracts. To test this point, 3 chromed powders of different ages were tried on a strongly sulphited extract, Mimosa D, with the following results:

	Percentage of non-tans		
Age of hide-powder	1.	2.	Average
(1) A few days	9.0	9.6	9.3
(2) 2 years	9.2	9.2	9.2
(3) 2½ years	9.4	9.5	0.45

This shows that alteration of the hide-powder on keeping need not be feared.

The Valuation of Dark Blood Albumin for Extract Clarification. J. JEDLICKA. *Gerber*, 1909, [35], No. 839, pp. 211-13.—Since the introduction by Gondolo of this material for extract clearing, it has become an important staple of increasing value. In quality it varies greatly; many

still believe it is correctly valued by a nitrogen determination, but the solubility is also to be taken account of. The author determines (1) moisture (2) ash, (3) solubility, (4) decolorizing power, (5) nitrogen. Water is determined by heating 2 gms. 4 hours at 100°; with longer heating, the weight increases and finally diminishes again. Good results have been lately obtained by distilling the water off with petroleum. In determining ash, the sample should be well ground to prevent loss by decrepitation. The ash is generally either about 3% or about 6%; only once was 4½% observed. Lack of solubility greatly lowers the value of the material. 5 gms. of the substance are rubbed with cold water in portions as long as the solution gives a ppt. with tannin. The insoluble part having been washed thus by decantation, is collected on a tarred filter, dried at 100° and weighed. It is desirable that blood albumin dissolve readily in cold water since the solution begins to ferment in a few hours. The decolorizing effect is tested by dissolving 5 gms. in 500 cc. water and adding 150 cc. of this slowly to 1 liter of unclarified oak wood diffusion liquor at 48°, warming to 70°, and quickly cooling to 30°. It is noted whether the supernatant liquor is clear or turbid, the depth of the sediment and the time of settling, all important factors in manufacture. The insoluble portion of the original albumin has often decolorizing power. To determine this, 2 or 3 gms. insoluble material (obtained by washing the required amount as ascertained by the solubility determination) are taken and the decolorizing effect compared colorimetrically with that of the soluble albumin which is made the unit; if for an equal weight, the effect is .5, the decolorizing power is 50%. Nitrogen is determined according to Kjeldahl, using mercury. To interpret the analytical results, the percentage of useful albumin is reckoned as 100 — water — ash — insoluble + efficient (decolorizing) insoluble.

TYPICAL ANALYSES

	Percentage of					
Source of material	Water	Ash	Insol.	N.	Decol power of Insol.	Useful
I. Austria Hungary	9.8	2.7	7.9	13.8	42	83.0
II. " "	8.7	3.2	6.1	14.1	51	85.2
III. Hungary	11.8	5.4	14.3	12.7	28	73.1
IV. Austria	12.6	3.5	5.6	14.0	63	81.9
V. Germany	13.2	6.1	21.4	12.5	52	65.0

Many firms claim their products to be superior because they produce only black albumin and do not merely obtain it as a by-product from the preparation of white blood albumin, a substitute for egg albumin. The author could find no essential difference in the two brands.

Catechol Tannins. HANS FRANCKE. From monograph, *Die Pflänzliche Gerbstoffe*, published by the author, Madgeburg; through *Collegium*, No. 377, pp. 330-6.—These tannins, coloring leather yellowish to reddish brown, are stable in solution with the exception of those from pine and oak

barks, which contain some ellago-tannic acid. Aside from these, the tannins of this class contain two components, one a colorless, easily soluble substance, rapidly browning in solution, the other a reddish dye stuff (phlobaphene) only soluble in hot water and depositing on cooling; it is however more soluble in presence of the colorless tannin. It has been found that by heating the colorless tannin of oak bark with water (Löwe) or alone (Etti), that it is converted into the red phlobaphene. Körner has shown that a similar result can be effected with quebracho, but only in presence of air, oxidation being necessary. These dye-stuffs can be reduced and several patents employ reducing agents for decolorizing. Mangrove shows an exceptional behavior and according to Körner contains no colorless tan-stuff; its tannin, which is dark-colored, is very soluble in water. The question arises whether in general, the phlobaphenes dissolved in tannin solutions have real tanning power. It has been established that tannin solutions are not homogeneous, but colloidal, or as Siedentopf and Zsigmondy call them, pseudo-solutions. These are suspensions, analogous to that of insoluble substances like ultramarine or arsenious sulphide in water. On addition of electrolytes, as salt, H_2SO_4 or alum, the insoluble dye-stuff is precipitated. Procter, v. Schröder and Bögh have found the insoluble sediment to have tanning power. Eitner has shown that it carries down much dissolved tannin from the liquor; when this is washed out, the residual dye-stuff produces a very inferior, brittle leather. Manstetten also finds that only the cold soluble tans are of value; these are fairly valued by the Löwenthal permanganate titration which gives less return for the oxidized poorer tannin in the dye-stuff.

Theory and Leather Industry. W. Eitner. (Address before Austrian Section). *Gerber*, 1909, [35], No. 818, pp. 198-200.—Practical tanning is based upon the accumulated experience of many times and people. The miscellaneous empirical precepts thus acquired may be properly ranged in a system by the scientist who takes account of practical conditions, but the pure theorist unfamiliar with these can contribute little to the solution of tanning problems. Nor are these to be solved on purely chemical lines alone. The great advances in practical leather-making during the last decades has been in the mechanical direction based to some extent on scientific principles. Knapp defined leather as an intimate adhesion of hide fibres and tannin, now called adsorption. We can expand this theory, employing certain conceptions of modern physiology. Organized substance is regarded as made of smallest particles called plasoms. A combination of such component particles of the hide fibrils with tannin is much more intimate than the superficial union assumed by Knapp. The author exhibited microscopic sections demonstrating the inner complex structure of the hide fibrils and these are described in the text. The fibrils are seen to be made up of a dense network of fine filaments which may themselves be considered as composed of plasoms to which the tannin molecules adhere. These plasoms are probably of different sizes in different hides and diffusion experiments have

shown that tannin molecules of various materials differ in size. A longitudinal section of calf hide, chrome tanned in two baths, after staining with hematin shows the complete penetration of the tannage within the fibrils, while the interfibril spaces remain vacant. This explains why chrome leather is not altered by boiling. Leather from the light colored easily diffusible quebracho tannin shows a similar section, while a preparation from the difficult soluble quebracho tannin, assumed to contain a larger molecule, shows little penetration, but a massive deposit on the surface in the sense of Knapp's definition.

Another science of importance to the tanning chemist is bacteriology. In aiming to preserve hide substance, the action of micro-organisms must be taken account of, as well as their possible beneficial action. In the purely chemical direction, the theorist has yet to differentiate the individual tannins and an exact tannin determination is still wanting.

The Interfibrillar Substance of Animal Hide. E. H. B. VANLIER. *Hoppe-Seyler's Zeitsch. f. Physiol. Chem.* [61], Hefte 2.—Rollet first separated from hide by solution in lime water an albuminous substance which may be regarded as the material surrounding and uniting the fibers. He and others class this substance with the mucoids, but Reimer, who named it "coriine," declared it to be entirely distinct from mucin. The author, however, believes it to be very closely related to the mucoid from sinew. He investigated fresh, thoroughly cleaned cow, calf and horse hide, extracting these daily with half saturated lime-water and water alternately as long as material was given up. The extraction was complete with cow and horse hide in a week, but required sometimes 4 weeks for the calf skin. Microscopic examination showed that the fibers could be easily separated but had not swollen in the least. The filtered extracts were precipitated by 5% acetic acid giving a voluminous stringy precipitate. This was dissolved in alkali and re-precipitated, and the product thus purified, the author calls "corio-mucoid." This acid, albuminous substance giving soluble compounds with the alkalies and alkali earths, resembles other mucoids not only in viscosity of solutions and solubility in excess of acids, but also in acquiring the power to reduce Fehling's solution after boiling some time with 1 to 2% HCl. It differs from tendo-mucoid from sinew in requiring less acid for precipitation, the precipitate being stringy and not flocculent.

ANALYSES.

Corio-mucoid	C	H	N	S
From cow hide I.	50.53	7.07	13.42	
" " " II.	50.05	7.75	13.97	1.84
" horse hide	50.51	7.91		1.49
" " "	49 98	7.92	15.58	
" calf hide	51.2	7.75	13.9	
Tendo-mucoid				
Leobisch	48.30	6.44	11.75	0.81
Chittenden and Giess.....	48.76	6.53	11.75	2.33
Cutter and Giess	48.04	6.67	12.47	2.20
Author			11.31	2.72

Levene obtained from tendo-mucoid by action of alkali a substance which he called glucothionic acid. The author prepared tendo-mucoid from the Achilles' tendon of kine and followed Levene's process for obtaining the Ba salt of above acid. The product gave no biuret reaction nor reduced Fehling's solution until after boiling with HCl, when $BaSO_4$ was also precipitated and a reaction for orcin could be obtained. On treatment of corio-mucoid in the same way (with 2% NaOH, separation of albumen by acetic and picric acids, preparation of Ba salt) a similar product was obtained giving the above reactions.

Negative Absorption and the Estimation of Plumping Effects of Acids on Hide-Powder and Pelt. E. STIASNY, *Gerber*, 1909, [35], Nos. 837-8, pp. 183-5, 198-9.—There is good support for the view that tanning is essentially an adsorption of colloidal matter by the surface of the hide fibres, the product becoming insoluble through secondary reactions. Adsorption does not always increase with colloidal character but is most marked with substances intermediate between the crystalloids and the marked colloids. With these last, the acting surface may take up solvent, but not the colloid, which then becomes more concentrated. This is called negative adsorption. The author has investigated the action of dry white hide-powder upon solutions of egg albumin (experiments by L. Gödel). It was found that the swelled hide contained 71.8% of water, and with ready chromed hide, 61.7%. Similar figures were obtained by first swelling the hide in excess of and then leaving it over night in the albumin solution; the results were 70.6 and 62.9% water. In these experiments it was assumed that no albumin was adsorbed by the hide and the water-content of the hide was computed from the results of the examination of the filtrate. The same principle was applied to the study of the swelling action of acids on hide-powder (experiments by P. Küchel). 5 gms. dry white hide-powder were moistened with 30 cc. water, left stand 1 hour, then shaken 3 min. with 70 cc. of egg albumin solution and 100 cc. of standard H_2SO_4. The liquid was then decanted, filtered and aliquot parts titrated and ashed.

Strength H_2SO_4	Percentage adsorbed (swelled hide = 100) H_2O	H_2SO_4
N	79.7	4.75
$^1/_2$ N	81.75	2.9
$^1/_4$ N	83.19	1.655
$^1/_{10}$ N	85.38	0.914
$^1/_{20}$ N	86.3	0.62
$^1/_{40}$ N	85.65	0.445
$^1/_{100}$ N	79.06	0.086
H_2O	68.53	

The adsorption of the water was increased by the acid, although not so much as to be expected, the maximum being reached at 1/20 N; with further concentration, the swelling decreased. The swelling with pure water was somewhat less than in the first experiments, due probably to use of a different hide-powder.

Similar experiments made upon butt, showed that the results obtained with hide-powder do not directly apply. The difference in action is probably due to structural difference in the more complex fiber of the butt. A maximum swelling was reached with a certain concentration of acid, when further concentration not only reduced the swelling, but finally produced contraction (negative swelling) designated in the table by minus signs. The butt then contained less water than when in contact with pure water alone.

EXPERIMENTS BY R. MATSUO, 1908.

Strength of acid	Gms. absorbed by 1 gm. butt. Water	Acid
4N sulphuric acid	—0.4219	0.485
3N " "	—0.1239	0.1483
2N " "	—0.0143	0.571
$1^1/_2$N " "	—0.0086	0.052
N " "	—0.0026	0.039
$^2/_5$N " "	0.0431	0.0179
$^1/_5$N " "	0.0422	0.0162
$^1/_{10}$N " "	0.0514	0.0157
$^1/_{25}$N " "	0.0312	0.0149
$^1/_{50}$N " "	0.0285	0.0123
4N acetic acid	—0.2375	0.323
2N " "	—0.0998	0.149
N " "	0.0534	0.058
$^1/_2$N " "	0.0739	0.043
$^1/_{10}$N " "	0.0694	0.0139
$^1/_{20}$N " "	0.0452	0.0102
$^1/_{50}$N " "	0.0218	0.0075

The Decolorizing and Clearing of Extracts. J. WLADIKA. *Gerber*, 1909, [35], No. 836, pp. 169-72.—This paper treats the subject in a general way without specific details. The principal difficulties to be overcome by the extract-makers are to avoid low tan-contents, bad color and insolubility in the product. The systems of decolorizing and clarifying may be classed as the hot systems, operating at a temperature of 60 to 100°, and the cold systems at 20 to 15°, with combinations of both at times. The hot system has the advantage of rapidity and compactness of plant, but gives less soluble product; it is therefore little used at present or else combined with the cold process. The chemicals used in the clarification in the cold systems are generally the secret of the factory; many are protected by patent, but few of these are practically used. For the hot system, blood albumin (Gondolo process) is used. An important factor in economical extract-making is the minimizing of the loss of useful tans in the sediment from clearing.

Concerning Kips. R. BUM. *Gerber*, 1909, [35], No. 837, pp. 185-6.—This hide comes from the zebu or humped ox (*Bibos indicus*) of India. In a land where animals are sacred, the skins are seldom injured dur-

ing life and as a rule, are carefully removed. Most defects originate during the curing processes. According to Evans in *Procter's "Principles,"* in the salting process the hides are repeatedly rubbed with a natural saline earth and dried in the open air. Another process, "arsenicing," is a treatment of the cleaned hides with a disinfecting bath for the purpose of preventing injury by insects, which is very liable in the hot climate. During the following drying, the frequent rains in the summer season occasion considerable loss from putrefaction. Long hair on the hide (winter hair) is a certain sign that the hide was not dried during the rainy period. The summer season does not injure the salted hides.

Brittle Grain in Leather. B. KOHNSTEIN. *Gerber,* 1909, [35], No. 840, pp. 225-6.—This frequent defect is more likely to occur in the denser parts of the hide as the rump and back, and less in the looser portions of the belly and neck. Even before the leather is made, the grain of the hide is sometimes apt to break unless care be exercised. The hides of sheep, goats, dogs and swine being looser in texture, are less liable to breaking of the grain than the firmer ox or calf skins. The sex and age of the animal are also of influence; the hide of a she-calf is more likely to give brittle grain than that of a cow or ox, especially when there has been too little fore-tannage. The conditions producing a fracture of the grain may be illustrated by taking two samples of sized writing-paper and glueing one to blotting-paper, the other to a thin board. On bending these the writing-paper (representing the grain) in the first case may be far stretched before breaking, while a slight flexure ruptures it in the second. The looser in texture the under-layer, the greater the resistance of the grain. If then the fibers be filled with tannin and loading materials, which produce a dense mass without hollow spaces, breaking may result. Certain tan-stuffs like valonia produce this result and the tanner must choose the proper material to secure an elastic grain with certain leathers. When soaps or fats fill the leather, the case is different, for these may be displaced on flexure of the leather. Also a strongly limed hide is less liable to grain fracture because of the open texture. A well-plumped hide has also greater grain resistance, but the acid should be thoroughly washed out. Another method of loosening the fiber and thereby lessening the tendency to grain fracture is by filling and distending the fiber with a suitable material and afterwards removing this. If a vegetable-tanned blank leather just taken from the hot-room for "burning in" tallow and paraffin or steam be tested, it will show a brittle grain due to contraction of the fibers by heat, especially if extracts were used. After impregnating with fat and stretching the fiber, the curried leather will show no inclination to fracture. If the fat be extracted with hot benzene, a faultless grain still remains in spite of the heat, for the fiber network remains expanded. This principle is applied in the manufacture of chrome patent leather. The practical tanner's device for overcoming brittle grain by stretching the leather by freezing illustrates the same idea.

When and How Should Chrome Leather be Re-Tanned With Vegetable Tanning Material? *Ledertechn. Rundschau*, 1909, No. 33, pp. 257-8.—In the early days of chrome tanning, the value of a vegetable after-tannage was greatly over-rated. When the chrome process was not so well understood as today, a flat and brittle product could at least be made softer and fuller by the combination process. In time, however, it was found that the disadvantages outweighed these gains. The fiber was loosened, but the after-tannage being too short to fill them, the leather remained loose and spongy, taking up water with ease. Any errors in the re-tannage made the product still worse and the combination process was gradually abandoned as the chrome leather improved.

In the manufacture of dyed chrome leather, however, the use of a vegetable after-tannage is desirable. The color of the leather is lightened and the absorption of dye is promoted. To attain these ends a slight superficial tanning is sufficient, so injury to the leather need not be feared. The tannage is best applied after milling with fat, the hides being first drawn through warm water and drained awhile on the horse. Sumach extract is the best material, 5 kg. to 100 kg. leather. This is dissolved in 50 liters water, then diluted to 100 liters of 30° temperature, filtered and then milled with the leather 1 hour, following with a thorough washing. An additional mordanting is desirable with 100 gms. tartar emetic in 70 liters water, milling 10 minutes. The dyeing with aniline colors follows.

Another exceptional employment of vegetable tanning is in the manufacture of a few technical chrome leathers requiring a certain fullness, density and water resistance, together with flexibility. The leather must be thoroughly freed from acid and then tanned as above, increasing the time of milling to 4 to 6 hours, and substituting quebracho for sumach, 850 gms. liquid extract to 1 kg. leather. The tannage begins with a 2° liquor, gradually increasing to 3 to 4°. An addition of 50 gms. salt to 1 kg. leather is of advantage. To make the product waterproof, it is strongly impregnated with solid fats or wax.

Lastly, as a case of need, this tannage may be resorted to in order to soften a chrome leather which for some reason has come from the currier hopelessly hard and brittle. The dry chrome leather is milled 5 to 10 minutes in a warm sumach solution of 3° B. after a slight washing, the leather is blacked and oiled on the grain.

"Wild" Grain in Drum Tanning. *Ledertechn. Rundschau*, 1909, No. 36, pp. 281-2.—This term is here applied to the coarse and irregular grain sometimes obtained in drum-tannage, special reference being made to sole-leather. The factors which contribute to this evil are generally prominent in drum tanning, namely, strong liquors, rapid motion and employment of chemicals to assist the process. The rational remedy is to subdue these and apply them cautiously. The fore-tannage should be gradual and thorough before going to the drum with the production of a smooth, tender grain. Above all, there should not be an excessive

plumping, which is a principal cause of the coarse grain. The hide is otherwise too stiff for the proper motion and acquires permanent folds and wrinkles. Furthermore, all chemicals for promoting swelling should be left out of the handler vats. In the drum-tannage itself, care should be taken that the liquors have the correct strengths and that the speed of rotation is moderate. If at the outset a marked grain has already formed, working on the machine is beneficial before proceeding further with the tanning. A light oiling of the grain is also at times advisable to moderate the action of the strong liquors.

Degras. *Ledertechn. Rundschau*, 1909, No. 36, p. 283.—A very serviceable degras may be made by saturating chamois-leather offal in the wheel with fish-oil, then layering 10 to 12 cm. deep in zinc-lined boxes and letting stand 12-15 hours. Boiling-water is then poured on with care to reach all the leather, which is then piled in a heap. The oxidation is so advanced in several hours that the degras may be squeezed out in presses. The product is left stand several days in the air with frequent stirring, and is then ready for use. The residual pressed leather may be used over.

PATENTS.

Leather-Splitting Machine. U. S. Patent No. 935,533. T. H. MAYO, Melrose, Mass.

Device for Supporting Hides. U. S. Patent No. 936,522. H. S. CROMBIE, Woburn, Mass.

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Mr. Edgar A. Prosser, care of Tanner's Dept., Vacuum Oil Co., 29 Broadway, New York City.

ASSOCIATE

Mr. F. C. Rose, care of Tanners' Dept., Vacuum Oil Co., 29 Broadway, New York City.

CHROMING OF HIDE-POWDER, ACIDITY OF HIDE-POWDER, AND THE RAPID COOLING OF TANNIN SOLUTIONS.[1]

By Chas. Eachus.

Realizing that the work of this committee would only be a preliminary step toward radical changes in our present official method, it was deemed best to first find out the opinions of American leather chemists on these subjects, based on experience.

The following letter was sent out:

As Chairman of the following Committees I hereby ask your collaboration in certain details, and would first state that I will not send out samples, but will ask each chemist to use different extracts that he has on hand, preferably solid ordinary quebracho extract, hemlock extract, or chestnut extract.

The committees are as follows:—

CHROMING OF HIDE-POWDER.

Power to call upon all members of the Association for collaboration. Decided that chrome alum has been proved to be equal and probably better than chrome chloride, but that the Committee should try the chroming with smaller volume of water against our official method. (Ten times the weight of water to weight of hide instead of twenty-five times is advised for trial.)

RAPID COOLING OF TAN SOLUTIONS.

Same Committee as "Chroming of Hide-Powder." The effect of rapid cooling to be determined upon non-tannin results as well as soluble solids.

ACIDITY OF HIDE-POWDER.

Same Committee as above, with power to recommend limits of acidity or a definite acidity, or further investigation as may be decided.

In regard to chroming of hide-powder would say that we should at present omit the comparison of chrome alum with chrome chloride and experiment with different methods of chroming hide-powder with chrome alum. Our present method of chroming hide-powder reads as follows:— "A quantity of hide-powder sufficient for the number of analyses to be made shall be pre-

[1] 1909 Committee Report.

pared in the following manner: Digest with twenty-five times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride."

The Chairman would suggest that you use ten times the weight of water to hide-powder chroming the usual way in comparison with the official method, and also compare this with chroming the hide-powder with chrome alum in a shaking machine for one hour similar to the I. A. L. T. C. method. The present method of chroming hide-powder according to the A. L. C. A. method is subject to wide variations. It means that a chemist must mix up his hide-powder with twenty-five times its weight of water, and chrome solutions, and shake occasionally until some time the next day. A method of chroming for one hour, or even one-half hour in a shaking machine, would probably be more uniform and reliable than the present A. L. C. A. method.

The rapid cooling of tanning solutions has been very well discussed in Mr. Wilson's report in the JOURNAL of the A. L. C. A., January, 1906. According to the work done then and conclusions there was little difference in insolubles, whether the extracts were analyzed after cooling, or after allowing to stand about twenty hours. No good reason has been given for allowing an extract to stand from twelve to twenty hours after it is dissolved, before analyzing, but much can be said against the procedure. Although some chemists claim that their laboratories maintain a temperature within the prescribed limits of analysis in both summer and winter, this is to be doubted, and in most laboratories there is a wide variation in temperature between the maximum of summer and the minimum of winter. If an extract is dissolved and allowed to stand over night in a laboratory in cold winter weather, it often happens that the temperature gets so low during the night that a large amount of insolubles are precipitated and these do not redissolve upon reheating. In summer the temperature is often so hot that the insolubles are held in solution. These conditions will cause a difference of three, or four per cent. in the insolubles of an ordinary quebracho extract.

If an extract is dissolved in hot water and cooled down to 20-25° C. inside of an hour and then analyzed, it is certain that more uniform conditions will be obtained.

The Chairman would like you to take different extracts, analyzing them according to the official A. L. C. A. method, and also try cooling the dissolved extract down to 20-25° C., under a stream of cold water, inside of one hour. Then analyze the rapidly cooled extract solution according to the official method. Also try the different methods of chroming hide-powder, as above suggested, with these extract solutions.

In regard to the acidity of hide-powder, you are requested to give the rapid method of determining acidity by Mr. Hough a thorough trial. This method can be found in the A. L. C. A. JOURNAL, August, 1909. This appears to be an accurate method, and will be a great help to further investigation of the acidity of hide-powder.

The Chairman would like to have results of your investigations and opinion not later than November 1st. If you cannot do any work, send your opinions, as they will be of value in the discussion of these subjects at the next meeting of the A. L. C. A.

Replies were received from practically all the collaborators and they are of value chiefly because they come from men who understand these subjects well, but who may not be at our meeting in Washington to discuss the questions involved.

Mr. W. K. Alsop:—

"My opinion in reference to some of the points you mention is as follows:—

Chroming of Hide-Powder.—I believe that ten times the weight of water to the weight of hide is just as good, or better than twenty-five times, providing the acidity of the hide is not too high.

Acidity of Hide-Powder.—I believe that there should be a definite acidity, or at least, only a small range allowed. We find that a hide using about 10 cc. of soda for 10 grams of hide, gives good results. A much lower acidity than indicated by this does not work so well, giving turbid filtrations with some extracts, and new bark solutions. We have found it satisfactory to add

soda to reduce the acidity of the highly acid hide, or to add acid to a hide with too low an acidity.

Rapid Chroming of Hide.—I do not believe that chroming one-half to one hour on a shaker will give as concordant results as our present method. I have made experiments along this line, and while short chroming with agitation is all right for some hide-powders, it does not work so well with others. I am inclined to believe that if the hide were soaked for say two hours in water, and then the chrome added, and the hide shaken for another hour, that the results would be much better.

Rapid Cooling of Tan Solutions.—Rapid cooling of tan solutions would be a great convenience many times, and I would be glad to see a comparison of two methods made by a number of chemists who are thoroughly familiar with the subject. I should have been very glad to have done some work on this matter if I had received your instructions in time to have done it. Judging from the results of such work as has been done, and from my own experience, I am inclined to believe that it might be as satisfactory as our present method, if the cooling of the solutions was done by some prescribed method."

Mr. A. W. Hoppenstedt:—

"In regard to the rapid chroming of hide-powder, it would seem that such a method would be desirable. However, it seems doubtful whether such a method would be adapted to various hide-powders. Chroming one-half or one hour in a shaking machine might work very well with some powders, but very poorly with others, whereas chroming for the length of time such as called for by the official method, seems to work well with all. The results obtained by the Committee in 1905, chroming hide-powder one-half and one hour were not very good. Whether the cutting down of the amount of water used for chroming, from twenty-five times to ten times the weight of the hide-powder taken, would be of any advantage in a method other than a rapid chroming method, seems questionable.

In the rapid cooling of tannin solutions there are three influencing factors which must be considered, viz: the rate of cooling, the manner of cooling and the temperature of the water

used for cooling. As a member of the Soluble Solids Committee in 1905, when Mr. Wilson was Chairman, I did a great deal of work on this subject. I am of the opinion that rapid cooling under the tap water will never give uniform results unless certain precautions are taken, as the temperature of the water is subject to such wide variations, being in the winter months often as low as 2° C. When rapidly cooling a hot tannin solution under a stream of water of this temperature, without much agitation, the portions of the solution next to the glass surface of the flask are cooled down far below 20° C., and this has the effect of precipitating a greater amount of reds in these portions, which do not redissolve, although the whole solution reaches a temperature of 20° C. The condition produced here is practically the same as the one you speak of in your letter when you say, 'If an extract is dissolved and allowed to stand over night in a laboratory in cold winter weather, it often happens that the temperature gets so low during the night that a large amount of insolubles are precipitated and these do not redissolve upon reheating.' If the hot tannin solution would be kept in constant motion during the cooling, so that the outside portions would not be excessively cooled, I think possibly good results would be obtained. Amongst the members of the Committee in 1905, I was apparently the only one who obtained more or less good results throughout, and I attribute this to the fact that I kept the solutions practically in constant motion during cooling. Nevertheless, I believe that water at a uniform temperature should be employed, preferably at 20° C., and not lower than 15° C. In case a satisfactory method could be worked out which would give good results, I would not be in favor of it as the only official method, and would only sanction it as an alternative method. There is no doubt that as an alternative method there would be many instances in a laboratory where it would come in handy.

In regard to Mr. Hough's method for determining the acidity of hide-powder, this method looks promising, although it is doubtful whether correct results are obtained by partly gelatinizing the hide or forming a gelatine solution by boiling, owing to the difficulty of accurately titrating a gelatine solution with phenolphthalein and NaOH."

Mr. W. A. Fox:—

"I am enclosing some results obtained in following out your committee work. I used four samples of extracts, as follows: One liquid hemlock extract, two ordinary quebracho extracts, three clarified quebracho extracts and four liquid chestnut extracts. All these extracts were analyzed officially, being kept at a temperature of 25° C. over night and cooled to 20° before the solubles were started. In addition these same extracts were dissolved in the morning and cooled rapidly to 20° under a tap before starting. Right here in my opinion is where the chief trouble in this method will occur, that is in the manner of cooling. I cooled mine under the tap with water about 80° C. in temperature with occasional shaking. I believe better results would be obtained if they were cooled more gradually, that is, have your cooling water at the start fairly warm, gradually decreasing the temperature, and never letting it get below say 15° C.

On those that I cooled rapidly, I noticed two things. First, they were lighter in color than those cooled officially. I noticed this not only on the original solution but also on the soluble solids, and the leather obtained shaking with hide-powder. Second, the reds when present seemed more finely divided than those cooled officially. In case of the hemlock this seemed to retard filtration, while in the ordinary quebracho the solution filtered more rapidly, but some went through the paper.

I used only two kinds of hide in this work, owing to the lack of time. However, my experience has been that the amount of water used on the hide causes very little difference, as long as you use enough so that the hide is fluid. Our experience has been that a hide-powder with an acidity of about 10 cc. N/10 NaOH for ten grams dry hide is best for general work, and hide of this acidity will flow easily with ten times its weight of water and at the same time take up the chrome more quickly and thoroughly than when twenty-five times the weight of water is added.

Hide No. 2, chromed in one hour, did not give very good results. The chrome was taken up very incompletely and the hide did not seem thoroughly wet with water. I do not believe that the hide will take up the chrome well until it is thoroughly wet, and I do not believe that one hour is time enough to do this. I

RESULTS OF W. A. FOX.

	Total solids. Per cent.	Soluble solids. Per cent.	Reds. Per cent.	Non-tannin hide No. I. Per cent.	Resulting tannin from hide No. I. Per cent.	Non-tannin hide No. II. Per cent.	Tannin from hide No. II. Per cent.	
1. Hemlock cooled officially.....	41.12	35.79	5.33	12.47	23.32	13.58	22.21	Solubles solids clear. Filtered very slow. Non-tannins, both Nos. I and II, turbid. No. II more so than No. I. Could not clear them up.
2. Hemlock cooled rapidly	41.28	35.41	5.87	12.59	22.82	13.82	21.59	Soluble solids filtered slower than No. I, but they were apparently no clearer. Non-tannins the same as No. 1.
3. Ordinary quebracho cooled officially ..	84.00	73.08	10.92	5.65	67.43	5.65	67.43	Soluble solids filtered slow, but were clear. Non-tannins clear.
4. Ordinary quebracho cooled rapidly...	84.04	74.33	9.71	5.65	68.68	5.75	68.58	Soluble solids filtered fairly fast, but were slightly turbid, and I could not clear them up. Non-tannins clear.
5. Clarified quebracho cooled officially..	88.25	88.09	.16	12.79	75.30	13.44	74.65	Soluble solids filtered fast and clear. Non-tannins clear.
6. Clarified quebracho cooled rapidly ...	88.25	88.21	.04	12.69	75.52	13.59	74.62	Soluble solids fast and clear. Non-tannins clear.
7. Chestnut cooled officially.....	41.59	40.81	.78	12.28	28.53	12.36	28.45	Soluble solids fast and clear. Non-tannins clear.
8. Chestnut cooled rapidly	41.55	40.89	.66	12.29	28.60	12.48	28.41	Soluble solids fast and clear. Non-tannins clear.

Hide No. I was chromed in the official manner, except that I used 10 times the weight of water.
Hide No. II was chromed one hour on the shaker with 10 times its weight of water.

have noticed that hide that I have started the day before does not take the chrome for several hours and then begins to act rapidly. Maybe if you let it stand for two hours and then shake it one hour on the shaker it will act better."

Mr. Fox gives the preceding table of analyses.

Mr. C. R. Oberfell:—

"In regard to chroming hide-powder I agree with your opinions that a smaller volume of water should be used and that the powder should be agitated while chroming for a comparatively short time.

Also, I believe that it would be well to cool the analysis infusions rapidly; principally for concordance and saving of time.

I have tried Hough's method for acid in hide-powder and find that it works satisfactorily. I think it would be better for concordance and accuracy to fix a definite acidity of hide-powder.

All of these opinions are of little value unless backed up with some data, but I have formed these opinions from observations while using the official method."

Mr. F. W. Alden:—

"I think it high time we were changing the mode of chroming hide-powder. In my opinion there should be just enough of water to float the hide-powder, so that only a very little clear liquor will appear at the top when the powder has settled. A shaking method would doubtless be a still further improvement. In regard to the rapid cooling of extract solutions, I should think some method of rapid cooling could certainly be much more easily controlled and that seems to be the main thing that is necessary."

Mr. F. O. Sprague:—

"Would say that in preparing the hide-powder we have used at different times, ten times the weight of water instead of twenty-five, and I can see no difference between them.

All your suggestions will, it seems to me, facilitate the work in a large laboratory, and I hope the collaborative work will allow of their adoption."

Mr. N. S. Loud:—

"The analyses, results of which are recorded on enclosed sheet, were carried on at a laboratory temperature of 74° to 75° F., and as I feel very sure, that those extracts which were dissolved over

N. S. LOUD'S RESULTS

Tan materials and methods of cooling	Total solids	Soluble solids	Insolubles	Non-tannins hide-powder methods: 10 × H_2O	A.L.C.A. 24 × H_2O	Drained 1 hr. 10 × H_2O	Soluble tannin
1. Solid quebracho dissolved and cooled down over night as per A. L. C. A. method	80.79	75.02	5.77	6.46	6.17	6.297	68.56
2. Solid quebracho dissolved and cooled to 68° F. and brought up to 75° F. inside 1 hour	80.49	76.96	3.53	7.08	6.17	6.296	69.88
3. Chestnut extract dissolved and cooled down over night as per A. L. C. A. method	35.89	35.58	.31	10.39	10.18	10.01	25.19
4. Chestnut extract dissolved and cooled to 68° F. and brought up to 75° F. inside 1 hour	36.03	35.74	.29	10.42	10.21	10.08	25.32
5. Chestnut extract dissolved and cooled over night as per A. L. C. A. method	38.77	38.62	.15	13.53	....	13.17	25.09
6. Chestnut extract dissolved and cooled to 68° F. and brought up to 75° F. inside 1 hour.	38.32	38.25	.07	13.55	....	....	24.70

1 and 2 same extract. 3 and 4 same extract. 5 and 6 same extract.

night, cooled down to about 68° F. toward morning, I allowed the solution which was cooled immediately to reach a minimum

RESULTS OF YOCUM-EACHUS LABORATORY.

	Total Solids	Soluble Solids	In-solubles	Hide-powder No. 1	Hide-powder No. 2	Hide-powder No. 3	Tannin using hide-powder No 1	Tannin using powder No. 2	Tannin using powder No. 3
Ordinary quebracho No. 1 cooled officially..	81.41	76.20	5.21	6.50	6.48	6.44	69.70	69.72	69.76
Ordinary quebracho No. 1 cooled rapidly...	81.68	26.70	4.98	6.70	6.66	6.60	70.00	70.04	70.10
Ordinary quebracho No. 2 cooled officially..	83.01	75.54	7.47	5.30	5.27	5.22	70.24	70.27	70.32
Ordinary quebracho No. 2 cooled rapidly...	83.13	76.45	6.68	4.89	4.82	4.80	71.56	71.63	71.65
Clarified quebracho cooled officially...	77.85	77.66	.19	13.11	13.14	13.19	64.55	64.52	64.47
Clarified quebracho cooled rapidly.....	77.77	77.66	.11	13.12	——	——	64.54	——	——
Chestnut extract cooled officially.....	38.63	38.39	.24	12.45	12.40	12.50	25.94	25.99	25.89
Chestnut extract cooled rapidly.....	38.72	38.53	.19	12.32	——	——	26.21	——	——

Hide powder No. 1 chromed officially.
Hide powder No. 2 chromed with ten times its weight of water.
Hide powder No. 3 chromed with ten times its weight of water in shaker one hour.

temperature of 68° and then just in a moderately warm place, until the laboratory temperature was reached.

It seems to me that this procedure was necessary in my case, in order to obtain comparative results. The most noticeable inference to be drawn from the experiments, is the fact that the drummed hide-powder shows the lowest non-tannins in all experiments and methods of preparation, but from what limited experience I have had with this method, would say that it requires considerable more washing than the other processes, or the A. L. C. A. method.

Blanks for hide-powder were run in all experiments. The drop in insolubles in the solid quebracho is very noticeable and also same tendency is shown in chestnuts."

Mr. Loud gives the preceding table of analyses.

The Yocum-Eachus Laboratory reports the preceding results, using different extracts, according to the general directions.

Mr. E. W. White:—

"I believe that it is better to chrome hide-powder one hour, using ten times its weight of water and three per cent. chrome alum.

In regard to rapid cooling, I cannot say much until I have more data. There seems to be considerable increase in the non-tannin figure when the extracts are cooled rapidly. If the change in the tannin is not too large, I should prefer the method of cooling rapidly for the reasons stated by you."

Mr. White gives the following analyses:—

1. Hide-powder + 25 times its weight water + 3% chrome alum 16 hours.
2. Hide-powder + 10 times its weight water + 3% chrome alum 16 hours.
3. Hide-powder + 10 times its weight water + 3% chrome alum shaken 1 hour.

	Ordinary quebracho cool over night	Ordinary quebracho cool in water 1 hour	Chestnut Extract cool over night	Chestnut Extract cool in water 1 hour
Total solids	87.87	87.85	42.07	42.29
Soluble solids	79.83	80.04	41.06	40.87
Insolubles	8.04	7.81	1.01	1.42
Non-Tannins				
H. P. (1)	10.83	11.36	14.49	14.75
H. P. (2)	10.67	11.15	14.48	14.92
H. P. (3)	10.98	11.25	14.52	15.01
Tannin (1)	69.00	68.68	26.57	26.12
Tannin (2)	69.16	68.89	26.58	25.95
Tannin (3)	68.85	68.79	26.44	25.86

Mr. F. H. Small:—

"The rapidly cooled solutions were cooled by being placed in running water at a temperature of about 16° C., being shaken at intervals during the cooling. So far as the results obtained go, it would seem that cooling an analysis solution rapidly has little if any effect on the insolubles. The differences between the insolubles found by cooling the solution in the official way and cooling it rapidly are within the limits of experimental error and this in spite of the fact that the insolubles seem to be of a considerably different character and appearance in the two cases. Moreover the time required for the filtration in the two cases was practically the same.

	Hemlock	Quebracho	Oak bark	Chestnut wood
Official	160 M.	155	120	50
Rapidly cooled	150	200	100	65

On the other hand in practically every case the non-tannin of the rapidly cooled solution is a trifle higher than the non-tannin of the officially cooled solution. The differences are not great, but they are so constantly in one direction that it seems at least possible that a higher non-tannin value is to be expected in the case of the rapidly cooled solution than in the case of the solution cooled according to the present official method.

Using hide-powder digested with only ten times its bulk of water and the usual amount of chrome alum and stirring for one hour, results are obtained which are consistently lower than the results obtained by the official method. This holds both for the officially prepared solutions and for the solutions rapidly cooled. This is moreover quite in line with the results shown in the report on some similar work of Reed, as published in the JOURNAL of the A. L. C. A. for November, 1908, page 326. The differences are not great but are consistently in one direction.

The acidity of the hide-powder used was estimated both by the direct method proposed by Bennett, by the indirect method proposed by Small, and by the boiling method proposed by Hough. The results obtained were as follows:

Direct	11.3
Indirect	12.2
Boiling	10.4

Of the three methods the boiling method proposed by Hough

is undoubtedly the most rapid of execution. The results so far as shown are, however, lower by this method. Which results are the most nearly correct I have had no opportunity as yet of trying to discover."

The following analyses were made in Mr. Small's laboratory by his assistant, Miss Worthen:—

	Hemlock		Quebracho		Oak bark		Ch. wood	
	Offi.	Rapid cooling	Offi.	Rapid cooling	Offi.	Rapid cooling	Offi.	Rapid cooling
Total solids	41.98	42.24	85.78	85.83	45.69	45.75	50.61	50.66
Soluble solids..	38.39	39.16	78.17	78.21	44.13	44.09	50.03	50.14
Insolubles	3.59	3.08	7.61	7.62	1.56	1.66	.58	.52
Non-tan[1].....	11.51	11.84	6.09	6.55	20.67	20.89	15.50	15.60
Total sol.-N. T.	30.47	30.40	79.69	79.28	25.02	24.86	35.11	35.06
Non-tan[2].....	11.23	11.69	6.04	6.21	20.39	20.52	15.23	15.20
Total sol.-N. T.	30.75	30.55	79.74	79.62	25.30	25.23	35.38	35.46

[1] Official. 44 gms. wet hide-powder containing 70.9% moisture or 12.8 gms. of absolutely dry hide-powder used to 200 cc. of solution.

[2] Rapidly chromed hide-powder. 44.2 gms. wet hide-powder containing 70.85% moisture or 12.9 gms. of absolutely dry hide-powder used to 200 cc. of solution.

While nothing is definitely decided by this committee work, some important points are brought in evidence. The chemists of the Elk Tanning Co., at Ridgway, say that an acidity requiring 10 cc. N/10 soda for 10 grams hide-powder is to be desired. Hough's method is quicker than the other methods of determining acidity and probably more accurate.

It would be a good plan in the future work on this subject, to take hide-powder with the above-mentioned acidity as a standard, compare it with other hide-powders, and use Hough's method of determining acidity. The chroming of hide-powder had better be continued for the present, according to the official method, but by using ten times weight of water instead of twenty-five.

The rapid cooling of tannin solutions affects such extracts as ordinary quebracho and hemlock, but clear extracts like chestnut and clarified quebracho do not show much difference in insolubles, when cooled rapidly or slowly. All future work in this direction could well be done on ordinary quebrachos and hemlock, trying out different methods of cooling.

All of these subjects require much more collaborative work, and data, but the Chairman hopes that this report will be of value as a foundation for future work.

SOME NOTES ON THE ESTIMATION OF ACIDITY IN HIDE-POWDER.

By D. L. Tucker.

It is my purpose to point out, in as short a space as possible, a few of the many difficulties which are experienced in the determination of the acidity in hide-powder by present known methods. In order to do this, I have taken the methods of Bennett (*Collegium,* No. 254, pp. 149-156,) which calls for direct titration with sodium hydrate, using phenolphthalein as indicator; that of Small (JOURNAL A. L. C. A., Vol. II., pp. 347-355, also Vol. III., pp. 75-78,) and which is about the same excepting that he adds an excess of the sodium hydrate and then titrates back with hydrochloric acid; that of Hough (JOURNAL A. L. C. A., for August, 1909, pp. 224-225, taken from *Collegium,*) which lays stress on the use of boiling water, or better, the boiling of the hide substance before titration, thereby gelatinizing the same; and a fourth method which is a modification of Bennett's method wherein sodium hydrate was added to bring down the acidity nearly to neutral and the solution left overnight before attempting the titration. These methods were compared by giving each a rather hasty, yet impartial trial.

Any and all of the present methods seem to offer considerable difficulty, especially in inexperienced hands, yet, the one proposed by Hough appears to be quite an improvement on the preceding ones in regard to giving a definite end-point or stopping place as we may call it. I have no doubt that any of the methods will give fairly approximate results when in experienced hands, but if I may take exception to the statement of Mr. Hough, I fail yet to find any method which will give results correct to 0.2 cc. However, in more experienced hands, these results might be gotten. The whole thing sums up to *What is correct, and where is the stopping point of the titration?*

Bennett's method is at the best a long, tedious operation if the titration be carried out with an ordinary amount of agitation and a careful estimation made. Again, with vigorous shaking, the color disappears rapidly as the sodium hydrate which penetrates the fibre slowly on standing, is forced into the substance. In a very few moments, a point is found which might easily be

taken for an end-point yet the titration may be carried much further by allowing more time for diffusion. Then, it becomes a question of how vigorous to agitate and how long to leave the mixture stand before calling the titration complete.

Small's method is somewhat better, in that he gives a specified time for leaving the solution stand before titrating the same. Then, in running back with acid, we experience almost as much of a difficulty in forcing the acid into the hide-substance as we do in the direct titration with sodium hydrate. Here, as in the Bennett method, the amount of agitation and the length of standing has considerable effect on the final results. Judging from the difference in titrations by allowing hide-powder to stand with excess of sodium hydrate added, have we reached the neutral point when we have complied with the directions of the method, if so, what neutralizes the alkali when the solution is allowed to stand longer?

Hough's method seems to be an improvement, in that it gives a direct titration with fairly good end-point. The hide substance being gelatinized by boiling with thorough shaking, an end-point may be reached where the color of the indicator holds fairly well. Since solutions of gelatine titrate very poorly with phenolphthalein and sodium hydrate, the assumption is that even these results would not be closer than 0.5 cc. The color change is not at all a marked one. This is not of sufficient importance to reject the method, however, but if we can get a method which will come within that limit of 0.5 cc. for the variation among different operators, then I think we have improved on the past methods. There can be no objection to this method as one which will give fairly concordant results, but there is a slight objection to it, in my mind, on the ground that a loss of acid takes place in adding boiling water or in the boiling. This is not substantiated, however, by any difference in results between the determination with boiling water and that by boiling for five minutes, but from my observations, boiling water when added causes a slight loss of acid. I did not carry out any experiments to confirm this, however.

A fourth method which is a modification of Bennett's method and which consists in addition of double the amount of water, then adding sodium hydrate to first color of phenolphthalein,

allowing the solution to stand over night and titrating to first heavy color without shaking. This works fairly well but acts the same as the Bennett method proper, in that a very slight amount of agitation will dispel the color. These results are concordant in a single operator's hands, but would undoubtedly vary widely in different hands. Then again, the question arises, since the color will not hold, have we determined the acidity?

Below will be found the results of my trials of these four methods with two different hide-powders:—

	Hide No. 1		Hide No. 2	
	Direct	Overnight	Direct	Overnight
Bennett.....	5.1 cc. N/10NaOH	7.4 cc.	18.5 cc.	18.2 cc.
	5.2 cc.	7.4 cc.	18.6 cc.	18.3 cc.
Small.....	6.6 cc.	7.6 cc.	19.5 cc.	20.6 cc.
	6.6 cc.	7.5 cc.	19.7 cc.	20.5 cc.
	Boiling water	Boiled 5 minutes	Boiling water	Boiled 5 minutes
Hough	5.7 cc.	5.9 cc.	19.3 cc.	19.5 cc.
	5.8 cc.	5.9 cc.	19.1 cc.	18.8 cc.
Bennett modified.....	5.7 cc.		18.8 cc.	
	5.7 cc.		18.9 cc.	

The equivalent of 6.5 grams of dry hide-powder, allowing 12% for moisture, was taken in all cases and 100 cc. water added, except in last, where 200 cc. was used.

In conclusion, allow me to state that from my observations, these difficulties appear to be due to several causes. The first of these is the great affinity which the colloidal hide substance seems to possess for ordinary indicators and which is best shown by the heavy color produced when the sodium hydrate strikes the outer surface of the hide substance and which gradually disappears. This may be demonstrated best by degreasing some hide substance with petroleum ether and then titrating the residue in water.

A second cause of difficulty seems to be in the tendency which the hide substance has for holding the acid, rather than in the slow penetrating power of the sodium hydrate. This may best be seen in the wide variation of the character of two hide-powders, one of which is low in acidity and in order to get the required acidity, acid has been added; and another which has originally been higher in acid but has been adjusted by sodium hydrate. They are very unlike in character.

The third cause appears to be due to the amount of acid present in the substance or to the salts formed in the reducing of the same. The reader may have observed that a high acid powder will titrate much better than a low one, at least this has been my experience.

There is apparently a large field open for some careful work on this subject, work which will bring out a method giving concordant results, at least for general tests on acidity of hide-powders.

ABSTRACTS.

Theory of Leather Formation. W. FAHRION. *Zeit. Angew. Chem.*, 1909, [22], Nos. 43-4, pp. 2083-97, 2135-44.—The results of additional experiments are described supporting the author's theory of tanning as an oxidation.

(a). *Chamoisage.*—Japan leather made by alternately watering the hide, working mechanically with rape-seed oil and exposing to the sun, has been pronounced by Paessler and by Eitner to be leather containing no tanning materials. The author, however, believes it to result from a chamoisage which is slight because of the low oxidizability of rape-seed oil. The iodine number of this is only 110, while cod-liver oil has 140 to 170, and linseed oil 160 to 180. The fat extracted from the leather by ether amounted to 5.25% and analysis showed that it had been oxidized:

	Rape-seed oil	
	Original	From leather
Acid number	2.8	60.9
Iodine number	100.1	36.0
Percentage oxy-acids (Insoluble in petrol. ether)	0.8	26.6

The essential tanning agents in chamois leather are held to be fatty oxy-acids which are chemically united with the hide, and therefore insoluble in ether. These "fixed oxy-acids" were determined in the degreased Japan leather by saponification with alcoholic potash, acidulating the aqueous solution of the product with HCl, and extracting in turn with ether, alcohol and petroleum ether.

	Per cent.	Iodine number
Soluble in petrol. ether	0.47	47.2
Soluble in ether	0.44	31.3
Soluble in alcohol	0.39	27.3

The total amount of fixed oxy-acids, 1.3% in the original leather, seems slight, but ordinary chamois leather shows similar small amounts. Doubtless the original hide from which the leather was made already contained some fixed oxy-acids, for hide-powder saponified as above yielded 0.7%.

The amount of actual "tans" present is further rated too high for another reason; the Japan leather degreased by ether, yields 0.7% alcohol soluble fat, which reduces the fixed oxy-acids to 0.6%. Experiments in imitation of the leather forming process were made upon hide-powder, first with rape-seed oil, which effected scarcely any tannage, and then more successfully with free fatty acids prepared from the oil, the idea being that in the auto-oxidation only the acid radical is active, and the removal of the glycerol promotes diffusion. After 2 months' exposure to air and maximum sunlight, a permanent yellowish product was obtained which, after extraction with ether and alcohol, gave 1.2% fixed oxy-acids, not removable by solvents until saponified. This the author calls "masked" oxy-acids.

Experiments were also made for the purpose of proving an oxidation during real chamoisage. In the practical process the 80% of water in the hide is expelled and replaced by the tanning agent through the excessive mechanical working. In laboratory experiment, the water is easier replaced by alcohol, and the hide then treated with alcoholic solution of the tanning fats. Of these four were tried, (a) commercial oleic acid and further the non-crystallizable free fatty acids from (b) rape-seed oil, (c) linseed oil and (d) whale oil. After soaking 24 hours in 10% alcoholic solution of these, the hide test-pieces were exposed to the air with occasional working to imitate the milling process for 2 weeks. The products all appeared to be leather which extracted with alcohol gave:

	(a)	(b)	(c)	(d)
Extracted by alcohol	23.1	21.4	11.8	16.2%
Iodine No. of extracted acids ..	84.9	66.7	57.1	73.2
Iodine No. of original acids	84.7	152.6	180.5	137.1
Oxygen reacting	....	2.6	1.3	1.35%

The reacting oxygen was computed from the iodine difference. Sample (a) after extraction was colorless and proved to be untanned on treatment with water; the others were yellow and remained permanent leather. The author distinguishes fat-tanned and chamoised leather, the former has its fibres separated by fat, which replaces the original water, but on extraction with solvents the leather reverts to hide. In chamoised leather there has been an auto-oxidation of the tanning material which is greater the more unsaturated the acids. Stearine, being saturated, gives merely a fat-tanned leather and the author has shown before (*Chem-Ztg.*, 1893, 1453,) that oleic acid, containing but one double union, is incapable of withdrawing oxygen from the air at ordinary temperature. The principal acid in rape-seed oil contains two double unions, linoleic acid from linseed oil three, and cod-liver oil has been shown to contain an acid of four double unions.

The author's hot water test (abstr. this JOURNAL, 1909, [III.] p. 60,) applied to Japan leather gave a resistance of 15 to 40%, varying with the sample. The conclusion is that this leather is chamoised to a certain

extent, but the greater part is unaltered hide. The next experiments described were made with liquid-free acids obtained from cod-liver oil with iodine number of 190.1, completely soluble in petrol. ether. Hide-powder in 5 gm. charges was saturated with this and exposed to air for 6 days, yielding finally

	Iodine number
2.88 gms. oxy-acids, sol. in petrol. ether	97.2
0.873 gm. oxy-acids, sol. in ether	73.5
0.596 gm. oxy-acids, sol. in alcohol	51.5

The extracted residual hide-powder had a water resistance (hot water test) of 72.8, much like commercial leather, and contained 0.77% increase in "masked" oxy-acids. Similar experiments made with alcoholic solution of the fat acid gave water resistances of 7.5 to 73.6, increasing with successive treatments, showing an oxidation to be essential to chamois; the final increase of "masked" oxy-acids was 1.43%.

Admitting a chemical oxidation of the fats necessary to chamois, those who support a physical theory of tanning might claim that leather results from a colloidal absorption of this oxidation product by the hide fibre. The author extracted the "masked" oxy-acids from his experimentally chamoised preparations and was unable to tan with them. He concludes that they are not tanning agents as such, and that chamoising is a real chemical process, the hide fibre itself being combined. The active tanning agents are peroxides which can exist free as shown by experiment. Liquid fat acids from cod-liver oil were exposed to air and sunlight for 4 months. The thick product was still totally soluble in alcohol but only partially soluble in ether and petroleum ether. The alcoholic solution mixed with an alcoholic solution of potassium iodide, on dilution with water gave a strong iodine reaction showing active oxygen. The reaction with the iodide was slow, increasing with time and strength of reagent. The peroxide acids thus obtained contained still unoxidized double unions as shown by iodine addition. From 10 gms. fat acid were obtained:

	I Soluble in petrol. ether	II Soluble in ether	III Soluble in alcohol
Peroxide acids	4.331	1.713	2.696 gms.
Iodine number	57.8	52.1	47.0

The active oxygen does not interfere with the determination of the iodine number. It also was determined (comparatively) from the iodine liberated by 0.5 gm. of each fraction amounting to 0.35, 1.55 and 1.25 cc. N/10 respectively. On standing, the peroxides gradually lose their power of liberating iodine, and the decomposition is entire on heating on the water bath. These peroxides were tested for tanning power by treatment of 1 gm. of hide-powder with 0.3 to 0.4 gm. in alcohol solution, leaving dry in the air for 6 days. The products were then extracted with alcohol and the recovered acid weighed, the difference being reckoned as "masked" oxy-acid.

	Ia	IIa	IIIa
Tan-stuff employed	0.364	0.358	0.348 gm.
Tan-stuff recovered	0.346	0.319	0.257 gm.
Iodine no. of last	57.8	50.8	53.2
"Masked" oxy-acids	0.018	0.038	0.089 gm.
Water resistance	17.3	50.8	42.6

Since the iodine number was not lowered there had been no auto-oxidation during the tanning; the peroxides themselves are thus proved to be direct tanning agents. If the peroxide acids be warmed with alcoholic alkali, the active oxygen disappears and they are transposed into lactones. Experiment showed that these were adsorbed by hide, but the product had a low water resistance. On repeating the tanning experiments with pieces of butt, it was found that the peroxide acids gave bright yellow, soft, elastic leather which was permanent on soaking in water; the product from the transformed peroxides remained brittle and deteriorated with water. The conclusion is that the lactones have no real tanning power.

Further experiments showed that it is essential that the peroxy-acid be in the free state to effect chamoisage. The alkaline salt and ethyl esters showed auto-oxidation, but effected little tannage. Engler having shown that turpentine oil furnishes peroxides on auto-oxidation, tanning experiments were tried with this agent. The best results gave a product resembling Japan leather of water resistance 22.3; alcohol extraction showed the presence of acids.

Since the acid group is essential to the tannage, it is concluded that the first phase of chamoisage is a salt formation, the peroxy-acids combining with the nitrogenous basic groups of the hide molecule. Stiasny's arguments against salt formation in leather are not considered conclusive (abstract, this JOURNAL, 1908 [III.] 246). That the amount of acid absorbed does not increase with the chlorination of acetic acid may be due to the lowering of diffusion by increase of molecular weight. That fatty acids are absorbed less than aromatic can be explained by the greater plumping effect which contracts the channels. That hide-powder takes up more acids from aqueous solution than alcohol does not disprove chemical action, for hydrolysis of the hide compound may do this in the same way, as oleic acid requires much more alkali for neutralization in aqueous solution than in alcohol (which corresponds to theory).

The second phase of the reaction is considered to be an oxidation of the hide component within the salt molecule analogous to the condensation of 2 molecules of aniline with quinone. The total reaction may be represented by

$$\underset{\text{hide}}{2X.NH_2} + \underset{\text{peroxy-acid}}{Y(O_2)_2COOH} = \underset{\text{leather}}{Y(OH)_2O.NH.X)_2COOH}.$$

(b). *Aldehyde Tannage.*—A discussion is given of the various theories that have been advanced. The author has regarded this tannage as analogous to chamoisage, the formaldehyde by the action of the air

forming a peroxide. Experiments however failed to prove this. He found cinnamic acid to be without tanning action, hence Nierenstein's conclusions based upon the action of cinnamic acid upon hide do not apply in this connection.

(c). *Vegetable Tannage.*—That hide may act chemically is proved by treatment with acetic anhydride. After extraction with alcohol, a product remains of water resistance 50.8, from which a volatile acid was separated of molecular weight 88 (acetic acid = 60) as determined by weighing the Na salt; the excess was probably due to other volatile matter. It is considered that the acetic acid has reacted with a carboxyl group of the hide, forming a mixed acid anhydride. Suida has found a similar reaction for wool. The author agrees with Stiasny in assuming both physical and chemical changes in leather formation, but believes the chemical stadium to be the principal and essential one. Conclusions drawn from physical changes have no bearing unless leather is formed which is not the case, for instance, in the adsorption of colloidal silicic acid by hide. A discussion follows of experiments made by the author in tanning with quinone prior to the publication of Meunier and Seyewetz's work in this line. He also obtained very insoluble leather, the water resistance being 92.3; genuine leather was produced, although lacking somewhat in softness and flexibility. The reaction is due to active oxygen, which attacks the nitrogen groups, for comparative determinations of the oxygen used up gave for cotton 0.2, silk 2.7, wool 8.5, hide-powder 5.3. In alcoholic solution a maximum reaction was obtained with 40 mgs. quinone to 1 gm. hide-powder of 14% water. From this the author computes 2122 to 2311 as limits for molecular weight of hide, which is regarded as still too low, since probably other reactions ensue. The leather reaction as in chamoisage is represented by

$$\underset{\text{hide}}{2X.NH_2} + \underset{\text{quinone}}{2C_6H_4O_2} = \underset{\text{leather}}{C_6H_4(ONH.X)_2} + \underset{\text{hydroquinone}}{C_6H_4(OH)_2}.$$

From the above molecular weight, the leather would then contain 2.3% quinone. A determination of the "masked" oxy-acids (increase) gave 2.1%, a fair agreement. In aqueous solution, a larger quantity of quinone is required for maximum tannage, because of the decomposition of a portion of the quinone by water. Experiments are described showing the loss of active oxygen in aqueous solutions of quinone on standing; the loss is accelerated by the action of light, air and alkalies, acid retards it. The action of quinone on hide-powder already tanned by aldehyde and by cod-liver oil peroxy-acids was tested; determinations of the absorbed oxygen gave: Hide-powder 5.1, aldehyde-tanned hide-powder 2.4, chamoised hide-powder 4.8. The reaction product of water on quinone was found to have little tanning power; it was absorbed by hide but gave a water resistance of only 25.9. Natural tanning materials, like oak bark and myrabolams were tested for quinone but no active oxygen could be found. If quinones act in vegetable tanning, they must be formed from the original phenols. Comparative tanning experiments with aqueous solutions of phenols and hide-powder gave water resistances of: phenol

23.6, pyrocatechin 36.5, resorcin 4.5 hydroquinone 4.7, pyrogallol 25.2, tannin 44.7; in alcoholic solution the action was but a fraction of the above. The author attributes to water a hitherto unrecognized role in vegetable tannage; the phenolic vegetable tans are oxidized by the water to quinones. This was confirmed experimentally by determining the active oxygen developed in solutions of hydroquinone as well as oak bark extract on standing, with exclusion of the air. Unlike Meunier and Seyewetz, the author found hydroquinone in aqueous solution to have some tanning action. With hide-powder and excluding the air, a product of water resistance 28.2 was obtained.

The quinone reaction however only composes a portion of vegetable tannage. Another phase is both physical and chemical. By catalytic action, the hide dehydrates the tan-stuffs, forming insoluble anhydrides, and these are deposited on the fibre. The whole product is a mixture of quinone and phlobaphene leathers, the first being the water-proof element, the latter a filler.

(To be Continued.)

The Formation of Phlobaphenes. M. Nierenstein and T. A. Webster. *Collegium*, 1909, No. 378, pp. 337-41.—Results are reported of a study of the formation of phlobaphenes from mangrove tannic acid through oxidation in solution by air, oxygen, and hydrogen peroxide. In all cases the tannin contents decreased with the increase in phlobaphenes. These last were estimated by the darkening of color. The precipitated oxidation product by oxygen gave anthracene on distillation with zinc dust. The oxidation product from potass. per-sulphate (β-phlobaphene) probably identical with the above, also gave anthracene. That obtained with hydrogen peroxide (α-phlobaphene), on distillation with zinc dust, gave di-phenyl methane. On boiling α-phlobaphene with dilute H_2SO_4, it was converted into the β-compound, then giving anthracene on distillation. The phlobaphene formation involves both oxidation and dehydration.

Preservation of Crude Hides. *Ledertechn. Rundschau*, 1909, No. 37, pp. 289-91.—Simple drying is effective, but the original condition of the hide cannot wholly be restored, and such hides are not suited for upper leather, moreover they may contain masked defects from imperfect drying. Hides are therefore generally preserved in most parts of Europe by impregnating with salt. In South America and Africa they are salted and air dried in addition. The wet salting process is used with light hides; these are first washed in fresh water, then strewn with salt, which is well rubbed in, and before bundling up they are strewn again with salt. In the pickling process, the hides are placed in a saturated salt solution containing sulphuric acid equal to 8 to 10% of the weight of the salt. In the East Indies, where salt is expensive, a natural saline earth containing glauber salt is rubbed into the hides (kips). In the same localities an antiseptic arsenic solution is used, followed by drying.

The Purification of Water by the Permutite Process. W. Appelius. *Ledertechn. Rundschau*, 1909, No. 38, pp. 297-9.—Dr. Gans has succeeded

in preparing an artificial zeolite of the formula $2SiO_2.Al_2O_3.Na_2O+6H_2O$. This is patented and manufactured by J. D. Riedel, Berlin, under the name of Permutite. By simple filtration through this material, hard water is deprived of lime, magnesia, etc., through exchange with the alkali. It is claimed that when expended, the filter may be regenerated by treatment with salt solution. The writer calls the attention of tanners to this process; he has found it effective in softening water but has made no test in regenerating the material.

The Tanning of Furs. *Ledertechn. Rundschau,* 1909, No. 38, pp. 299-300. —This is a simple operation, but only sound, healthy skins should be used. After thorough washing and cleansing, they are spread flat on a table and a mixture of 2/3 powdered alum, 1/3 salt rubbed into the flesh. This is repeated with each skin in turn and they are then folded or rolled up according to size and laid away in a tub, guarding against drying. In summer, they may be covered with water. After 3 days they are taken out and treated again as before. This procedure is repeated until the tanning is complete, which is recognized by the hide appearing entirely white on sections, without any transparency. The skins are then rinsed, drained, flattened on the table while half dry, and rubbed with a little glycerine, also with oil when hard, and then hung up to dry. The grease may be removed from heavy furs by rubbing on the hair side with clay paste, drying and beating.

School of the Tanner; Uniformity in Liquors. A. SCHMIDT. *Le Cuir,* 1909, [2], Nos. 16, 18, 20; pp. 363-5, 411-3, 459-61.—Regularity of process is the main factor in good tanning and a systematic control of the strength of the liquors secures this. In practice the specific gravity as determined by the hydrometer is generally relied upon. This is often misleading, for not only do different tanning materials vary in gravity for the same strength in tans, but the gravity is also affected by the acids, and the problem is indeterminate. This is particularly the case in the ancient process, where the acids are developed by fermentation and fluctuate according to conditions, season, etc. In the modern process when the liquors are sterilized by the addition of an antiseptic and artificial acids are regularly added, the combined gravity as shown by the hydrometer may be relied upon for control.

PATENTS.

Vacuum Evaporator. U. S. Patent No. 937,114. TOZABURO SUZUKI, Sunamura, Japan.

Process of Tanning Skins and Hides. U. S. Patent No. 937,720. HENRY SCHMID, Mulhausen, Germany. Consists in impregnating the prepared skins and hides with the solution of a basic salt of a sesquioxid, and then treating the impregnated skins and hides with an alkaline solution of sodium zincate.

Leather Splitting Machine. U. S. Patent No. 937,765. JAMES BUSHFIELD, Haverhill, Mass.

Evaporating Apparatus. U. S. Patent No. 939,143. S. M. LILLIE, Philadelphia, Pa.

Tannin-Containing Extract and Process of Producing Same. U. S. Patent No. 940,394. A. KUMPFMILLER, Hocklingsen, Germany. The process of producing a tan-liquor easily soluble in water, consisting in preparing a vegetable tannin-containing extract, purifying a waste cellulose sulphite solution by heating same and then pouring it into a chamber from which the air is partially exhausted, eliminating thereby sulphurous acid, concentrating the liquor and precipitating insoluble calcium sulphite, separating the latter by filtration, adding carbonate of sodium to the solution, transforming thereby the bisulphite of calcium into sulphite of calcium and the calcium salts of organic acids into sodium salts, filtering and adding hydrochloric acid to the filtrate, mixing the remaining solution with the vegetable tannin-containing extract.

Evaporating Apparatus. U. S. Patent No. 940,473. JOHN PARKER, Philadelphia, Pa., assignor to Kestner Evaporator Co.

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